

Materials Balance for Chlorophenols
Level I - Preliminary

JRB Associates, Inc.
McLean, VA

Prepared for

Environmental Protection Agency
Washington, DC

4 Feb 80

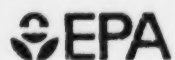


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Agency

Office of
Toxic Substances
Washington, DC 20460

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Toxic Substances



Materials Balance for Chlorophenols

Review
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Level I - Preliminary

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16. ABSTRACT This report presents a Level I materials balance study on 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. Areas of major interest were production quantities, producers, consumption amounts and emissions to air, land, and water related to the above sources. The estimated production quantities in 1976 of the compounds studied were as follows: 2-chlorophenol, 9000 kkg; 4-chlorophenol, 9800 kkg; 2,4-dichlorophenol, 39,000 kkg; 2,4,5-trichlorophenol, 6300 kkg; 2,3,4,6-tetrachlorophenol, 1,800 kkg; and pentachlorophenol, 22,000 kkg. Waterborne emission was considered to be the main pathway of chlorophenols release to the environment because of the physical characteristics of these chemicals. The estimated quantities of aquatic emissions associated with the chlorophenols studied were as follows: 2-chlorophenol, 430 kkg; 4-chlorophenol, 650 kkg; 2,4-dichlorophenol, 870 kkg; 2,4,5-trichlorophenol, 105 kkg; 2,3,4,6-tetrachlorophenol, 67 - 160 kkg; pentachlorophenol, 840 - 1400 kkg. Throughout this report, estimations and assumptions were made in places where needed information was not available. Bases for these estimations were stated and defined. Recommendations for further studies were also made.		
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FINAL REPORT
LEVEL I MATERIALS BALANCE:
CHLOROPHENOLS

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF PESTICIDES AND TOXIC SUBSTANCES
SURVEY AND ANALYSIS DIVISION
Task No. 5
Contract No. 68-01-5793
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Submitted: February 4, 1980

THE FINAL REPORT PRESENTED HERE RESULTED FROM A LEVEL I MATERIALS BALANCE STUDY ON CHLOROPHENOLS. THE RESULTS WERE BASED ON AN ANALYSIS OF LITERATURE SUPPLIED BY EPA. ALTHOUGH SUPPLEMENTARY INFORMATION UNDOUBTEDLY EXISTS, OBTAINING IT WAS OUTSIDE THE SCOPE OF THIS TASK. THE LEVEL I REPORT IS INTENDED TO SERVE AS A FOCUS OF DISCUSSION AND AS A BASIS FOR FUTURE MATERIALS BALANCE STUDIES; IT IS NOT MEANT TO BE A DEFINITIVE STUDY.

LEVELS OF ENVIRONMENTAL MATERIALS BALANCES

Materials balance studies are performed at three levels or depths of study and effort. In general the study of a chemical proceeds sequentially through these three levels. Particular chemicals are assigned to be studied at one of the levels on the basis of availability of information. The three levels are described below:

Level I:

A LEVEL I MATERIALS BALANCE requires the lowest level of effort and involves a survey of readily available information for constructing the materials balance. Ordinarily, many assumptions must be made in accounting for gaps in information; however, all are substantiated to the greatest degree possible. Where possible the uncertainties in numerical values are given, otherwise they are estimated. Data gaps are identified and recommendations are made for filling them. A Level I materials balance relies heavily on the EPA's Chemical Information Division (CID) to provide readily available information. The first draft of most Level I Materials Balances is completed within a three to six week period; CID literature searches are generally completed within two weeks. Thus the total time required for preparation of the initial draft of a Level I materials balance ranges from five to eight weeks.

Level II:

A LEVEL II MATERIALS BALANCE involves a greater level of effort, including an in-depth search for all information relevant to the materials balance. The search includes all literature (concentrating on primary references), contacts with trade associations, other agencies, and industry to try to uncover unpublished information, and possibly site investigations. Uncertainties and further data needs are identified in the Level II report. Recommendations for site sampling needs for Level III are also identified.

Level III:

A LEVEL III MATERIALS BALANCE generally involves the assimilation of new data obtained. It builds on the Level II literature searches and reviews of industrial production data by filling in data gaps through site visits and monitoring. The data generated for a Level III Materials Balance are intended to be statistically valid and have known confidence values. Level III Materials Balances are also intended to provide a basis for regulations or legal proceedings.

ABSTRACT

This report presents a Level I materials balance study on 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. Areas of major interest were production quantities, producers, consumption amounts and emissions to air, land, and water related to the above sources. The estimated production quantities in 1976 of the compounds studied were as follows: 2-chlorophenol, 9000 kkg; 4-chlorophenol, 9800 kkg; 2,4-dichlorophenol, 39,000 kkg; 2,4,5-trichlorophenol, 6300 kkg; 2,3,4,6-tetrachlorophenol, 1,800 kkg; and pentachlorophenol, 22,000 kkg. Waterborne emission was considered to be the main pathway of chlorophenols release to the environment because of the physical characteristics of these chemicals. The estimated quantities of aquatic emissions associated with the chlorophenols studied were as follows: 2-chlorophenol, 430 kkg; 4-chlorophenol, 650 kkg; 2,4-dichlorophenol, 870 kkg; 2,4,5-trichlorophenol, 105 kkg; 2,3,4,6-tetrachlorophenol, 67 - 160 kkg; pentachlorophenol, 840 - 1400 kkg. Throughout this report, estimations and assumptions were made in places where needed information was not available. Bases for these estimations were stated and defined. Recommendations for further studies were also made.

TABLE OF CONTENTS

Abstract	<u>Page</u>
List of Tables	v
List of Figures	vi
List of Abbreviations	vii
Executive Summary	viii
1.0 Introduction	1-1
1.1 Physical Properties of Chlorophenols	1-3
2.0 Monochlorophenols	2-1
2.1 2-Chlorophenol	2-2
2.1.1 Production of 2-Chlorophenol	2-5
2.1.2 Uses	2-8
2.1.3 Summary	2-11
2.2 4-Chlorophenol	2-11
2.2.1 Production	2-11
2.2.2 Uses	2-16
2.2.3 Summary	2-24
3.0 2,4-Dichlorophenol	3-1
3.1 Flow Diagram for 2,4-Dichlorophenol	3-1
3.2 Direct Production of 2,4-Dichlorophenol	3-1
3.2.1 Amounts Produced	3-1
3.2.2 Amounts Imported	3-5
3.3 Emissions Due to Production and Imports	3-5
3.3.1 Emission Due to Production	3-5
3.3.2 Emissions Due to Imports	3-11
3.3.3 Emissions Due to Other Sources of Production	3-12
3.4 Emissions Due to Consumption and Use	3-12
3.4.1 2,4-Dichlorophenoxyacetic Acid (2,4-D) Manufacture	3-12
3.4.2 Timber Processing	3-16
3.4.3 Leather Tanning and Finishing	3-17
3.4.4 Impurities in 2,4-D	3-17

	<u>Page</u>
3.4.5 Degradation of 2,4-D in the Environment	3-17
3.5 Summary	3-17
4.0 2,4,5-Trichlorophenol	4-1
4.1 Direct Production of 2,4,5-Trichlorophenol (2,4,5-TCP)	4-1
4.2 Amount Imported	4-7
4.3 Emissions Due to Production and Imports	4-8
4.3.1 Emissions Due to Production	4-8
4.3.2 Emissions Due to Imports	4-11
4.3.3 Emissions Due to Other Sources of Production	4-12
4.4 Emissions Due to Consumption and Use	4-12
4.4.1 Amounts of 2,4,5-Trichlorophenoxyacetic Acid and Derivatives and Trichlorophenol Sodium Salt Produced	4-12
4.4.2 Emissions to Air	4-13
4.4.3 Emissions to Water	4-13
4.4.4 Emissions Due to Disposal of Solid Residues	4-14
4.4.5 Degradation of 2,4,5-TCP in Derivatives	4-15
4.4.6 Direct Use of 2,4,5-TCP	4-16
4.5 Summary	4-17
5.0 Tetrachlorophenol	5-1
6.0 Pentachlorophenol	6-1
6.1 Environmental Flow Diagram for PCP	6-1
6.2 Production	6-4
6.3 Consumption and Uses	6-6
6.3.1 Wood Preservation	6-7
6.3.2 Pressed Board and Insulation Board Manufacture	6-7
6.3.3 Other PCP Uses	6-7
6.4 Emissions to the Environment	6-12
6.4.1 Production of PCP	6-12

	<u>Page</u>
6.4.2 Formulation of PCP Products	6-17
6.4.3 Distribution and Storage of PCP and PCP Derivatives	6-17
6.4.4 Releases from Uses	6-18
6.5 Summary of Pentachlorophenol Materials Balance	6-24
7.0 Major Emission Locations	7-1
8.0 Data Gaps	8-1
8.1 Identification of Major Producers and the Annual Production Quantities of Chlorophenols	8-1
8.2 Level of Chlorinated Phenols Contained in the End Products as Contaminants	8-1
8.3 Information on Environmental Emissions	8-2
List of References	

LIST OF TABLES

<u>Table</u>		<u>Page No.</u>
1.1	Physical Properties of Commercially Important Chlorophenols	1-4
2.1	Uses of 4-Chlorophenol (1976)	2-25
3.1	Production and Sales of 2,4-Dichlorophenol (kkg)	3-3
4.1	Producers of 2,4,5-Trichlorophenol	4-3
4.2	Production and Imports of 2,4,5-TCP and its Acid, Acid Derivatives and Salts	4-4
4.3	Molecular Weights of 2,4,5-TCP and its Derivatives	4-5
6.1	Pentachlorophenol Producers	6-4
6.2	Estimated Supply and Demand for Pentachlorophenol	6-5
6.3	Quantities of Wood Products Treated with Pentachlorophenol, 1975	6-9
7.1	Major Emission Locations	7-2

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1.1	Process Flow for Chlorination of Phenol	1-2
2.1	Producer and Production Sites for 2- and 4-Chlorophenol	2-3
2.2	Flow Diagram of 2-Chlorophenol	2-4
2.3	Materials Balance for 2-Chlorophenol (kkg)	2-12
2.4	Flow Diagram of 4-Chlorophenol	2-13
2.5	Locations of Quinizarin Production Facilities	2-18
2.6	Materials Balance for 4-Chlorophenol (kkg)	2-26
3.1	Flow Diagram for 2,4-Dichlorophenol, 1976 (kkg)	3-2
3.2	Producers and Production Sites for 2,4-D	3-13
3.3	Materials Balance for 2,4-Dichlorophenol (kkg)	3-18
4.1	Flow Diagram for 2,4,5-Trichlorophenol	4-2
4.2	Production Schematic for 2,4,5-Trichlorophenol Production by Hydrolysis of 1,2,4,5-Tetrachlorobenzene	4-9
4.3	Materials Balance for 2,4,5-Trichlorophenol (kkg)	4-18
5.1	Materials Balance for Tetrachlorophenol (kkg)	5-2
6.1	Flow Diagram for Pentachlorophenol (kkg)	6-2
6.2	Pentachlorophenol Producers	6-3
6.3	Geographical Distribution of Wood Preserving Plants in the U.S.	6-8
6.4	Geographical Distribution of Hardboard Manufacturing Facilities in the U.S.	6-10
6.5	Geographical Distribution of Insulation Board Manufacturing Facilities in the U.S.	6-11
6.6	Production Process for Pentachlorophenol	6-14
6.7	Materials Balance for Pentachlorophenol (kkg)	6-25

LIST OF ABBREVIATIONS

2,4-DCP	2,4-dichlorophenol
2,4-D	2,4-dichlorophenoxyacetic acid
PCP	pentachlorophenol
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
2,4,5-TCP	2,4,5-trichlorophenol
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
MCP	monochlorophenol
DCB	dichlorobenzene
POTW	Publicly-Owned Treatment Works

Numbers in parentheses are references; see reference list of report.

Superscript numbers are footnotes; see the end of the table or figure.

EXECUTIVE SUMMARY

This Level I materials balance reports on emissions due to production and use of several representatives of the class of chlorophenols. The compounds specifically designated by the Task Order for study are 2-chlorophenol; 2,4-dichlorophenol; 2,4,5-trichlorophenol; 2,3,4,6-tetrachlorophenol; and penta-chlorophenol. We have also included 4-chlorophenol in this study.

The chlorophenols are solid compounds with slight water solubility. They have low vapor pressures. The production and uses of the individual compounds will be summarized below. In almost all cases, production, use and emissions data were not readily available so that the values presented are based on estimates and extrapolations.

The figures included with this summary present the data and emissions estimated for each compound for the year 1976.

Monochlorophenols

2- and 4-Chlorophenol are each synthesized by two major methods: chlorination of benzene and hydrolysis of dichlorobenzene. The total estimated amounts of each isomer produced in 1976 were: 2-chlorophenol, 9000 kkg; 4-chlorophenol, 9800 kkg. Phenol chlorination accounted for an estimated 78% of 2-chlorophenol and 87% of 4-chlorophenol, with the rest produced by dichlorobenzene hydrolysis. Emissions to water were the largest category of emissions due to production: 190 kkg/year in 1976 for 2-chlorophenol; 210 kkg/year for 4-chlorophenol.

In the absence of direct data, we estimated the major consuming process of monochlorophenols to be further chlorination to yield higher chlorophenols. Emissions to water from these uses were approximately the same as those due to production: 190 kkg/year for further chlorination of 2-chlorophenol; 180 kkg/year for 4-chlorophenol in 1976.

2,4-Dichlorophenol

2,4-dichlorophenol is synthesized by two routes: chlorination of phenol (estimated 80%; 31,200 kkg in 1976) and chlorination of chlorophenols (estimated 20%; 7,800 kkg). Emissions from these processes were almost entirely aqueous: 819 kkg/year estimated emissions to water; 39 kkg/year to air. The other major source of estimated emissions was production of the pesticide 2,4-D from 2,4-dichlorophenol. This process released an estimated 2.1 kkg to the air and 42 kkg to water in 1976. Breakdown of 2,4-D in the soil could be a major source of land emissions, but further data are necessary to evaluate this point.

2,4,5-Trichlorophenol

2,4,5-Trichlorophenol is synthesized by hydrolysis of 1,2,4,5-tetrachlorobenzene. In the absence of direct data, production was estimated to be 6500 kkg in 1976. Diazotization of 2,4,5-trichloroaniline produced an estimated 10 kkg in 1976. Emissions due to production were estimated to be 94 kkg to water, 7 kkg to air and 6 kkg to land in 1976. In several consumption processes, total emissions were estimated to be significant but allocation to an environmental medium was not possible. For instance, we estimated that all 433 kkg used in 1976 as fungicides may be released to air + land + water, but the distribution could not be estimated.

2,3,4,6-Tetrachlorophenol

The tetrachlorophenol was produced in the smallest amount of the chlorophenols studied: 1800 kkg in 1976. It is formed by chlorination of phenol in the presence of a catalyst. Its major use (estimated 67% of production) was as a wood preservative. Compared to the other chlorophenols, releases from tetrachlorophenol production were relatively small. Leaching from preserved wood poles could be significant, at 770 kkg in 1976.

Pentachlorophenol

Pentachlorophenol showed a 1978 production of 22,000 kkg. It is produced by chlorination of phenol using a catalyst. An estimated 12 kkg were released to air during this process, along with 660 kkg to water. It has many uses based on its biocidal and preservative properties. A leading source of estimated emissions was its use in homes and gardens (110 kkg emitted to water, 380 kkg emitted to soil). A major source of release could be from utility poles treated with PCP, as a result of PCP leaching and evaporation. A preliminary estimate indicated that this source could emit up to 9600 kkg to land and water.

The locations with the greatest concentration of chlorophenol-producing capacity were Midland, Michigan, and Sauget, Illinois.

This report contains many best-guess estimates of important figures, such as production amounts and emission factors. This is because much of the desired information was proprietary and therefore confidential. Access to this information would be necessary for more detailed analysis of chlorophenols emissions.

The materials balances of the chlorophenols are summarized in Figures ES-1 through ES-6. Each figure refers to the most recent year for which data were available: 1976. In calculating the summary equation for each materials balance, the terms "Amount Consumptively Used" and "Amount Non-Consumptively Used" are the amount of compound entering the process minus the emissions due to the process. This prevents double-accounting of emissions.

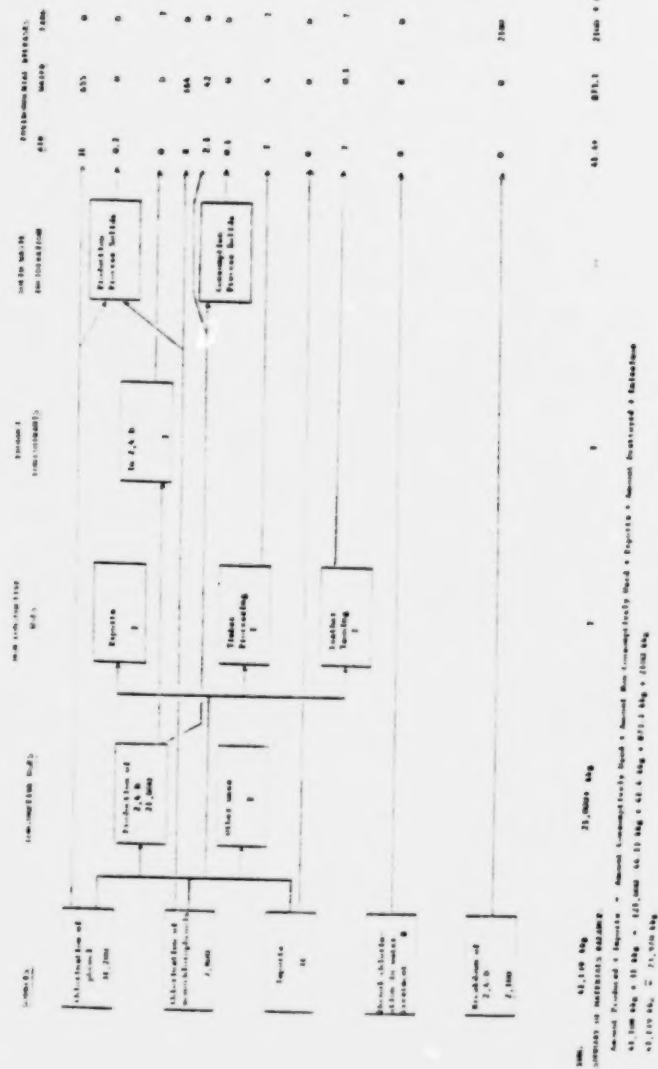


Figure ES-3 Materials Balance for 2,4-Dichlorophenol (kg)

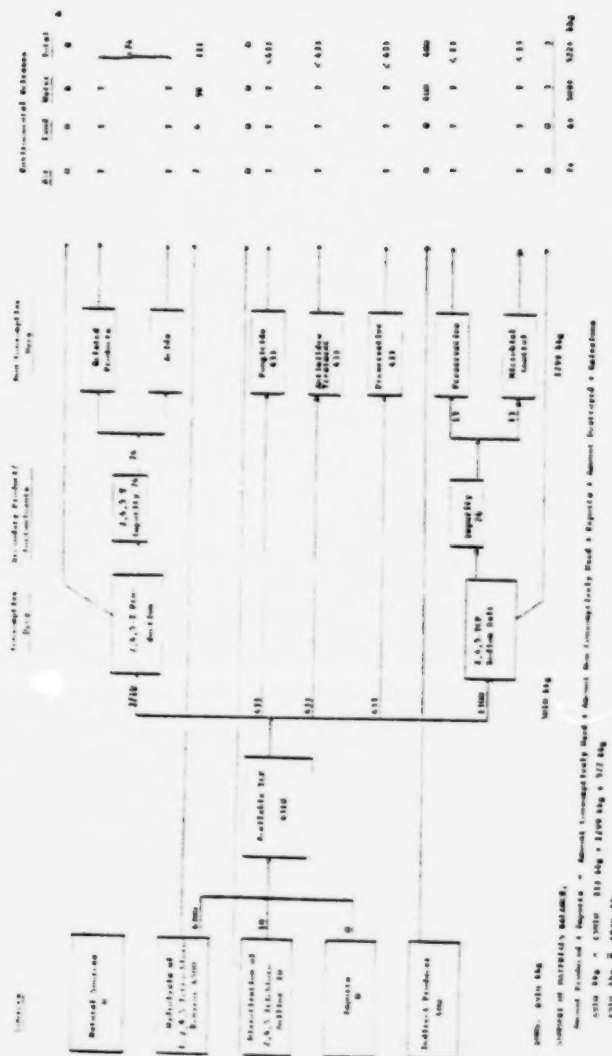


Figure ES-4 Materials Balance for 2,4,5-Trichlorophenol (kg)

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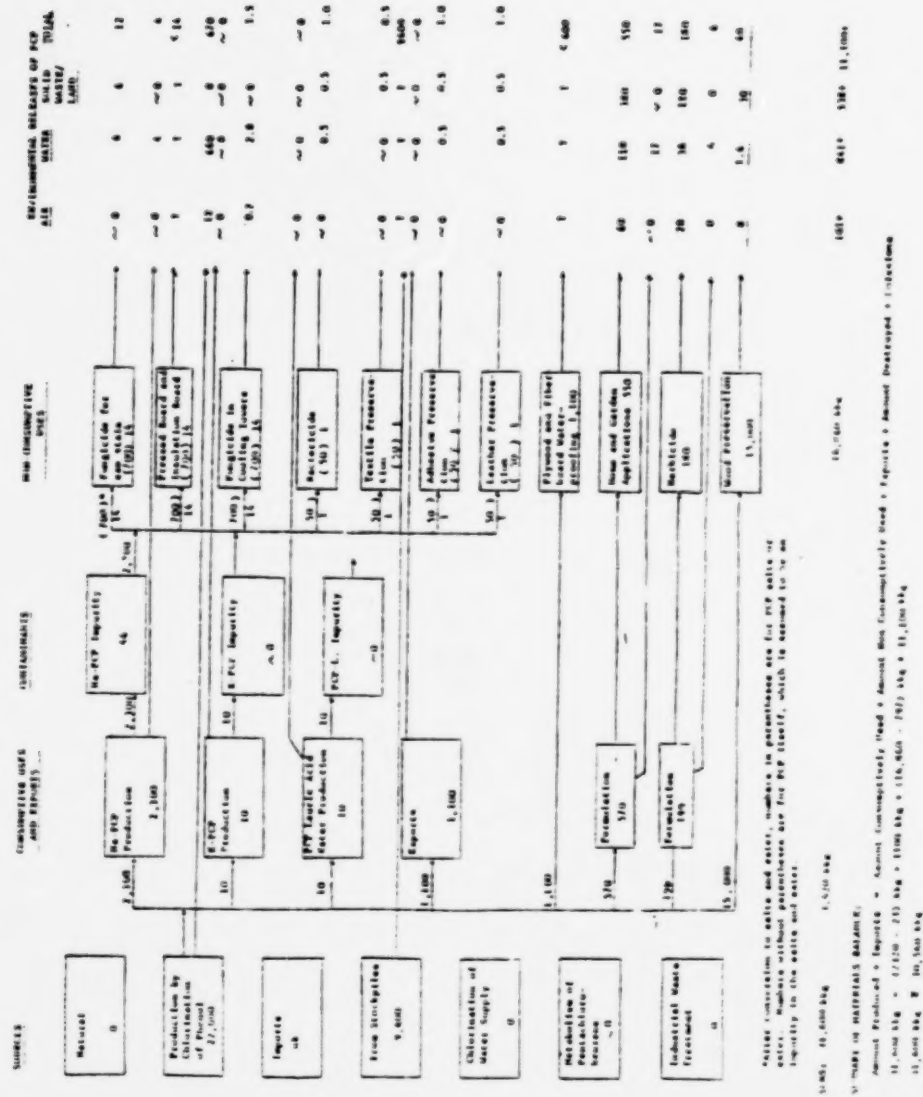


Figure ES-6 Materials Balance for Pentachlorophenol (kkg)

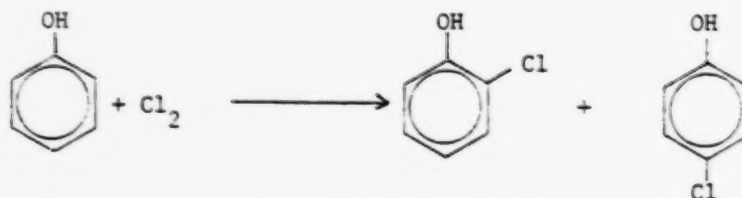
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1.0 INTRODUCTION

This report has been prepared in response to a task order from the United States Environmental Protection Agency (EPA) for a Level I materials balance study on chlorophenols. A draft report was submitted September 7, 1979, and has been revised and rewritten as this report. The specific compounds listed in the Task Order are 2-chlorophenol; 2,4-dichlorophenol; 2,4,5-trichlorophenol; 2,3,4,6-tetrachlorophenol; and pentachlorophenol. In order to accommodate this multiple materials balance, a separate chapter is presented on each compound. Within each chapter are sections on emissions due to production and imports, emissions due to consumption, and emissions due to other sources. Each chapter will present the compound's overall materials balance, and the text and footnotes will describe how derived values were obtained.

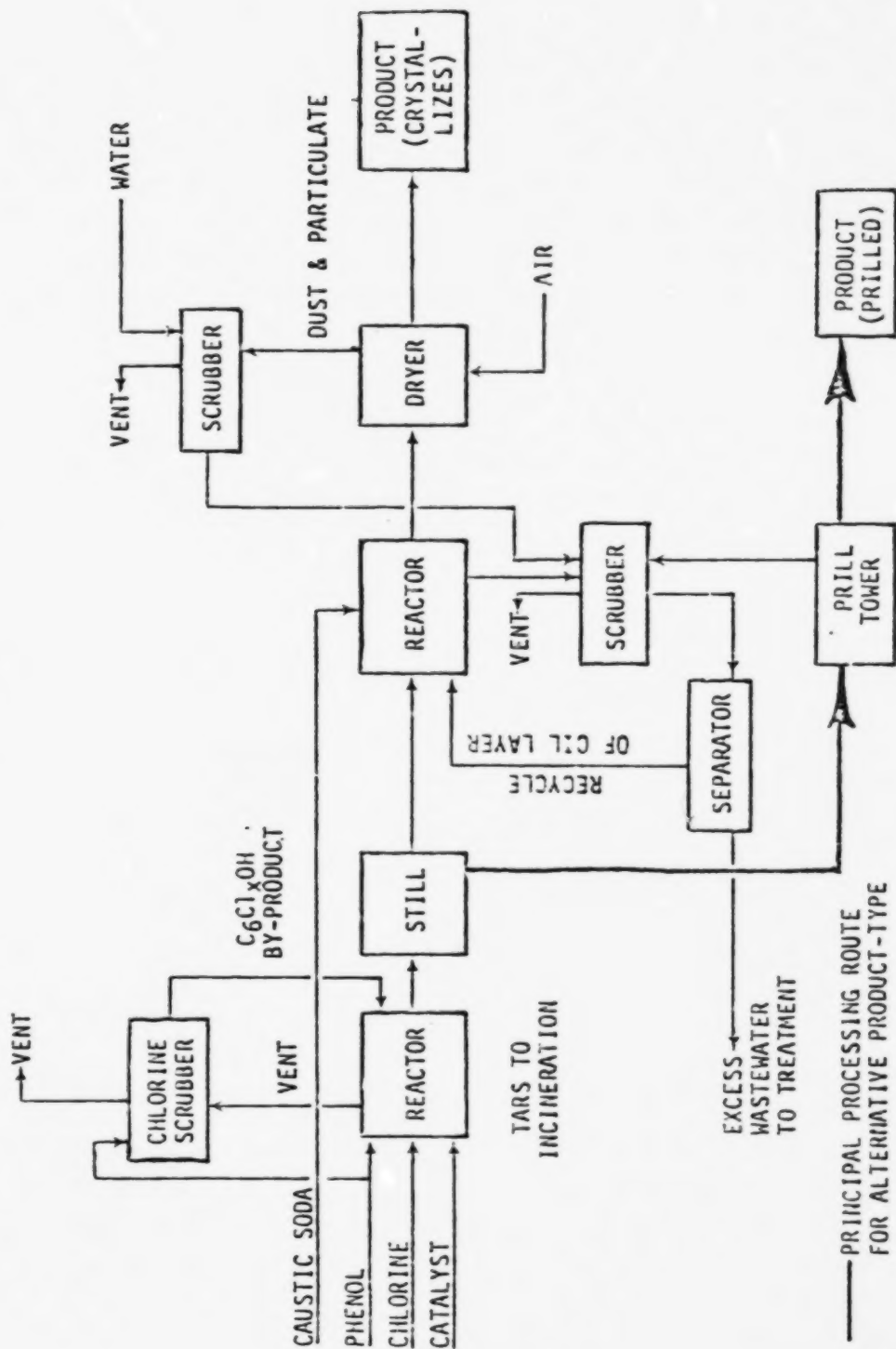
Chlorophenols are used as wood preservatives, fungicides, herbicides, molluscicides, mold inhibitors, antiseptics and disinfectants. In addition, they are also used as precursors for the synthesis of dyes, pigments and pesticides. They form a class of synthetic organic chemicals used as pesticides and chemical intermediates at a rate exceeding 100 million pounds per year (EPA, 1975a).

All of the chlorophenols discussed in this report are synthesized by the same basic process: chlorination of phenol by molecular chlorine:



The reaction proceeds readily, and the chlorophenols produced will serve as reactants for further chlorination reactions. These reactions are carried out industrially by the process flow shown in Figure 1.1. The respective chapters will refer back to this figure in discussions of emissions. (A prill tower produces aggregated (prilled) product by passing it counter-current to water mist in a column.)

FIGURE 1.1 PROCESS FLOW FOR CHLORINATION OF PHENOL.¹



1.1 PHYSICAL PROPERTIES OF CHLOROPHENOLS

The physical properties of the most important chlorophenols are summarized in Table 1.1. They are solids at room temperature and all have a pungent, medicinal odor. They are at most slightly soluble in water. Their salts, however, are soluble in aqueous base. The volatility of the compounds generally decreases, and the melting and boiling point generally increase, as the number of chlorine atoms substituted on the benzene ring increases. Vapor pressures are relatively low.

TABLE 1.1 PHYSICAL PROPERTIES OF COMMERCIALLY IMPORTANT CHLOROPHENOLS¹

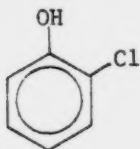
Compound Property	4-Chlorophenol	2,4-Dichloro- phenol	2,4,6-trichloro- phenol	2,4,5-trichloro- phenol	2,3,4,6-tetra- chlorophenol	pentachloro- phenol
Melting point (°C)	40-41	43-44	68	68	69-70	190
Boiling point (°C)	219	210-211	246	245-246	164/23mm	309-310
Dissociation constant (K_a) at 25°C	6.6×10^{-10}	2.1×10^{-8}	3.8×10^{-8}	3.7×10^{-8}	4.2×10^{-6}	1.2×10^{-5}
Solubility (g/100g) ² Water (25°C)	2.71	partial	insol.	partial	0.10	14-19 ppm
Temperature at which the vapor pressure equals 1mmHg	49.8	53.0	76.5	72.0	100.0	0.0005 mm Hg (20°C)

¹SOURCES: EPA (1975a) and Weast (1977)

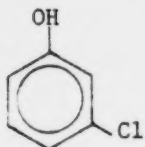
²When quantitative data were not available, qualitative characterizations were presented as a general guide.

2.0 MONOCHLOROPHENOLS

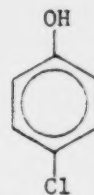
There are several monochlorophenols. The types of monochlorophenols and their molecular structures are given below:



o-chlorophenol
2-chlorophenol



m-chlorophenol
3-chlorophenol



p-chlorophenol
4-chlorophenol

The types of monochlorophenols which are most commonly found in commercial and industrial use are the o- and p- isomers. They are both produced from the same chemical process and are used in the same manner. The m-chlorophenol is rare as the conditions required for its formation are difficult to achieve. This discussion will focus on the two common forms of monochlorophenol.

The information available on the monochlorophenols is as follows:

1. The production quantity of quinizarin in 1976 was reported at 7.79×10^2 kkg (USITC). Quinizarin is a product made from the reaction of p-chlorophenol with phthalic anhydride.
2. An estimated 9000 kkg of 2-chlorophenol were produced in 1976 (Tracor-Jitco, 1977c). The basis of this estimation was not discussed in their report.
3. Percentages of o-dichlorobenzene and p-dichlorobenzene used respectively in the production of 2-chlorophenol and 4-chlorophenol were obtained from the Stanford Research Institute estimates (Stanford Research Institute, 1975).

Other than the above data, information on other production processes, production quantities, consumption quantities and emissions were unavailable. Many assumptions and estimations were made in order to describe the environmental flow of monochlorophenols and possible emissions quantities. It should be noted that these derived quantities were not necessarily based on actual data, but

were meant to serve as illustrations of the possible flow of monochlorophenols in the environment and potential emissions to air, land and water released by the producing and consuming industries.

More monitoring data are needed to properly assess the source and quantity of emissions of monochlorophenols from these industries. Information on production processes, production quantities and consumption quantities are also needed in further studies.

The discussion on monochlorophenols is divided as follows:

Section 2.1 - 2-chlorophenol

2.1.1 - Production of 2-chlorophenol

2.1.2 - Uses

2.1.3 - Summary

Section 2.2 - 4-chlorophenol

2.2.1 - Production of 4-chlorophenol

2.2.2 - Uses

2.2.3 - Summary

2.1 2-CHLOROPHENOL

2-chlorophenol was produced in 1976 by Dow Chemical Company in Midland, Michigan and by Monsanto Company in Sauget, Illinois. The annual production capacity of Dow Chemical plant was reported from 5,000 to 7,500 kkg; the Monsanto plant had an annual production capacity of 10,000 to 12,000 kkg; the Monsanto plant had an annual production capacity of 10,000 to 12,000 kkg (Tracor-Jitco, 1977c). Figure 2.1 shows the locations of 2-chlorophenol and 4-chlorophenol production plants in the United States. Figure 2.2 shows a flow diagram for 2-chlorophenol.

FIGURE 2.1 PRODUCERS AND PRODUCTION SITES FOR 2 - CHLOROPHENOL AND 4 - CHLOROPHENOL

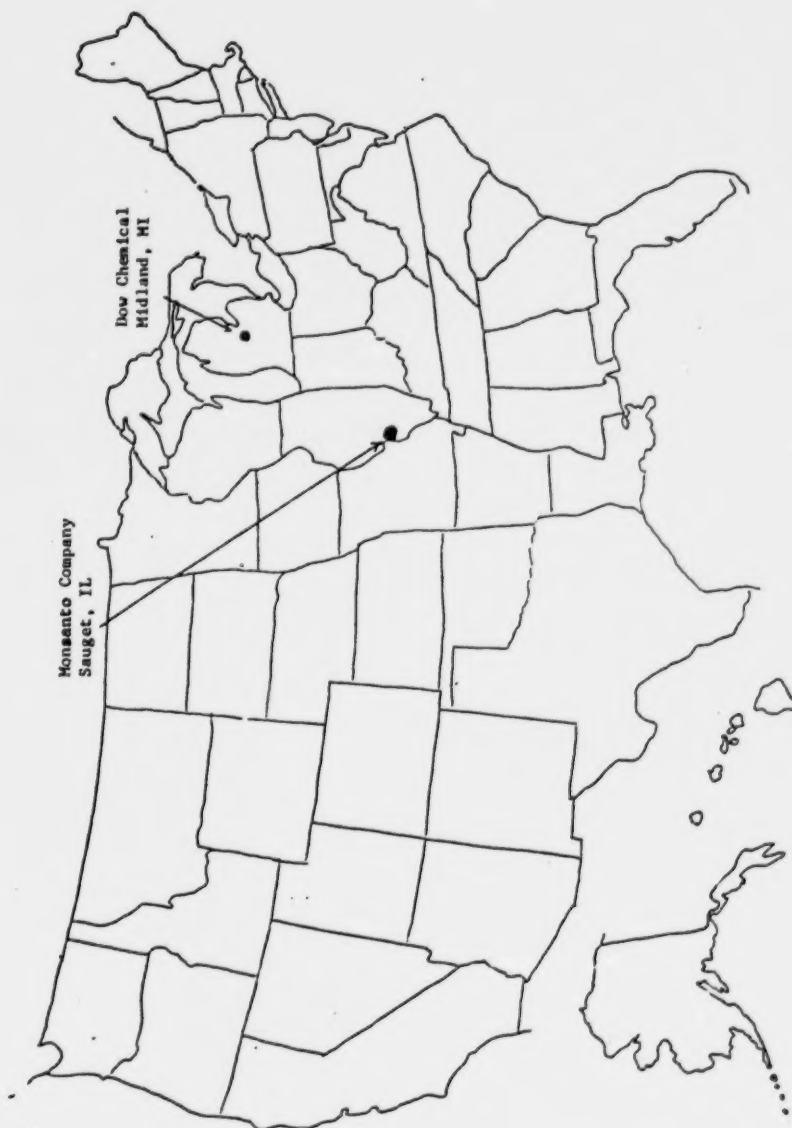
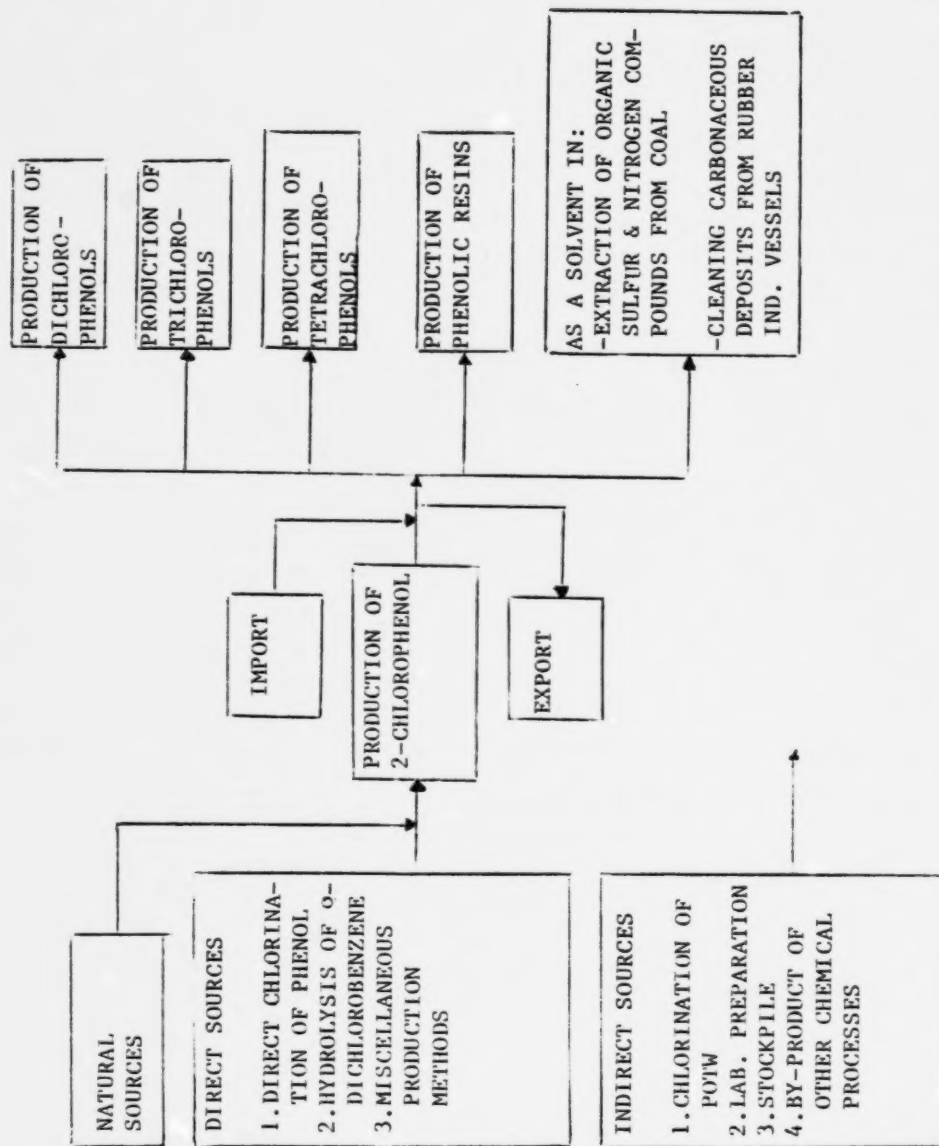


FIGURE 2.2 ENVIRONMENTAL FLOW DIAGRAM OF 2 - CHLOROPHENOL

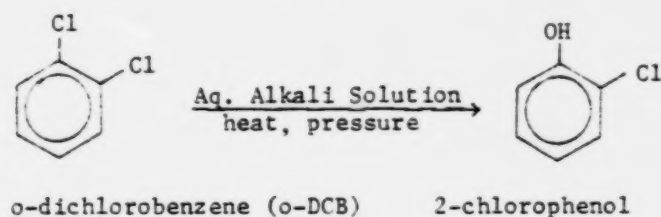


2.1.1 Production of 2-chlorophenol

There are several methods of preparation of 2-chlorophenol which have been used by industry. Direct chlorination of phenols has been the most widely used process, although hydrolysis of chlorinated benzene is also feasible. Other exotic synthetic routes are applicable but do not contribute greatly to the total production of 2-chlorophenol. We will discuss the direct chlorination and the hydrolysis method of 2-chlorophenol production.

2.1.1.1 Hydrolysis of Chlorinated Benzene

2-chlorophenol (2-CP) can be produced by the hydrolysis of o-dichlorobenzene (o-DCB). Generally, hydrolysis is carried out in aqueous alkali solutions at high temperatures and under pressure (PEDCo, 1979b). This process has an average yield of 86% (PEDCo, 1979b). This estimation was based on the yield range of 85 to 90% given by Kirk-Othmer (1969). The main reaction in this process is:



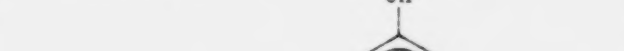
Stanford Research Institute has estimated that in 1976, 12% of the total production of o-dichlorobenzenes was consumed in the production of 2-chlorophenol (SRI, 1975). The total production of o-dichlorobenzene in 1976 was reported to be 2.2×10^4 kkg (USITC). This production volume was based on the quantities reported by the manufacturers. Therefore, the total quantity of 2-chlorophenol produced by the hydrolysis of o-dichlorobenzene can be calculated by multiplying the following factors:

- 1) The percentage of o-dichlorobenzene used in the production of 2-chlorophenol,
- 2) Total production of o-dichlorobenzene,

- That is:

The unreacted materials are usually recycled for other uses.

Direct chlorination of phenol with molecular chlorine is the most widely used production process for 2-chlorophenol. In this preparation method, 4-chlorophenol is formed as a chief product and 2-chlorophenol is produced as a by-product. The distribution of these two products was estimated to be 45% 2-chlorophenol and 55% 4-chlorophenol. This estimation is based on the chemistry of phenol. The -OH group of phenol is a strong ortho/para director, and therefore, upon chlorination of phenol, the reaction proceeds to produce 2- and 4-chlorophenol. Based on similar processes such as bromination and sulfonation of phenol, it was assumed that the yield of the para product would be greater than the yield of the ortho product (Morrison and Boyd, 1973). A yield of 45% ortho product and 55% para product was estimated based on the slower reactivity of chlorination compared to that of the bromination.



phenol + Cl₂ → 4-chlorophenol (55% yield) + 2-chlorophenol (45% yield)

The total production of 2-chlorophenol in 1976 was estimated to be 9,000 kkg (Tracor-Jitco, 1977c). The basis of this figure was not reported. Assuming that no other production methods of 2-chlorophenol, except the hydrolysis method, contribute any significant quantity to the total production of 2-chlorophenol, the total production of 2-chlorophenol from the direct chlorination of phenol was estimated by subtracting the total annual production of 2-chlorophenol from the production quantity derived from the hydrolysis method. Therefore:

$$(9 \times 10^3 \text{ kkg}) - (2 \times 10^3 \text{ kkg}) = 7 \times 10^3 \text{ kkg 2-chlorophenol}$$

2.1.1.3 Indirect Production Sources of 2-chlorophenol

The most probable inadvertent source of 2-chlorophenol production was the chlorination of municipal water containing chlorophenol precursors such as phenol or cresol. It was estimated that the annual production of 2-chlorophenol from the treatment of municipal water amounted to 15 kkg in 1976 (Versar, Inc., 1977a). There were some uncertainties in the derivation method for this estimation and more monitoring data are needed to properly assess this indirect production source of 2-chlorophenol.

2.1.1.4 Imports

The quantity of 2-chlorophenol imported was not reported in 1976. It was estimated that the amount would be negligible compared to the total production quantity.

2.1.1.5 Other Potential Production Sources

Production of 2-chlorophenol as a by-product of other chemical production processes (except the direct chlorination of phenol) was not mentioned in the literature. Stockpiles of 2-chlorophenol were not reported or mentioned in the past. Laboratory preparations of 2-chlorophenol were estimated to be minimal ($< 0.1 \text{ kkg}^a$); these would not contribute significantly to the total production amount.

^a JRB estimate.

2.1.1.6 Emissions of 2-Chlorophenol Due to Production

No information on the emissions of 2-chlorophenol to the environment was readily available. We estimated that most of 2-chlorophenol emissions during production would be released to water, and that the aquatic emission factor would be approximately the same as for 2,4-dichlorophenol emissions. This estimate was based on similar aqueous solubility properties and similar production processes for the two chemicals.

The estimated emissions of 2-chlorophenol to water were estimated by multiplying the total production quantity of 2-chlorophenol by the emission factor obtained for 2,4-dichlorophenol (see Section 3.3.1.1.2). Therefore:

$$(9.0 \times 10^3 \text{ kkg}) (2.1 \times 10^{-2} \text{ kkg/kkg}) = 1.9 \times 10^2 \text{ kkg 2-chlorophenol to water}$$

Atmospheric emissions were estimated to be 5% of the aquatic discharge (see Section 3.3.1.1.1), and were calculated as follows:

$$(1.9 \times 10^2 \text{ kkg}) (0.05) = 9.5 \text{ kkg 2-chlorophenol emitted to air}$$

Emission to land was estimated to be negligible.

2.1.2 Uses

Most of the 2-dichlorophenol produced in 1976 was consumed in the production of higher chlorinated phenols; a small amount was used in the production of phenolic resins. 2-Chlorophenol has also been utilized as a solvent in the extraction process of organic sulfur and nitrogen compound from coal, and as a cleaning solvent in the removal of carbonaceous deposits from vessels and tanks of the rubber industry (Kirk-Othmer, 1969; Tracor-Jitco, 1977c).

Information on the quantity of 2-chlorophenol consumed in the above uses was not available. We estimated that in 1976, 99% of the total production of 2-chlorophenol was consumed in the production of higher chlorinated phenols and the remaining 1% accounted for all minor uses (phenolic resin formulation, solvents).

2.1.2.1 Production of Higher Chlorinated Phenols

2,4-Dichlorophenol and 2,6-dichlorophenol are produced by direct chlorination of 2-chlorophenol. Trichlorophenols and tetrachlorophenols can also be formed if further chlorination is carried out (Kirk-Othmer, 1969). Pentachlorophenol is produced by chlorination of trichlorophenols and tetrachlorophenols at higher temperature condition and in the presence of catalyst (see Section 6.1).

It was estimated that in 1976, 99% of the total production of 2-chlorophenol was used in this production process, but this percentage was only estimated for calculation purposes and was not based on literature sources. Additional information is needed to confirm this estimate. The total quantity of 2-chlorophenol used in the production of higher chlorinated phenol was then estimated as follows:

$$\left[\begin{array}{l} \text{total annual} \\ \text{production of} \\ \text{2-chlorophenol} \end{array} \right] (0.99) = \left[\begin{array}{l} \text{quantity of 2-chlorophenol} \\ \text{used in the production of} \\ \text{higher chlorophenols} \end{array} \right]$$

$$(9.0 \times 10^3 \text{ kkg}) (0.99) = 8.9 \times 10^3 \text{ kkg}$$

2.1.2.1.1 Emissions of 2-Chlorophenol from the Production of Higher Chlorinated Phenols

Again, no information on the emissions of 2-chlorophenol to the environment was available. We assumed that most of 2-chlorophenol emissions would be associated with the aqueous stream, based on the physical characteristics of the compound. An estimated emission factor of 2.1×10^{-2} kkg/kkg was appropriate for calculation purposes by analogy to 2,4-dichlorophenol (Section 3.3.1.1.2). The aquatic emission of 2-chlorophenol from this production process was then estimated by multiplying the total consumption quantity by the emission factor. Therefore,

$$(8.9 \times 10^3 \text{ kkg}) (2.1 \times 10^{-2} \frac{\text{kkg}}{\text{kkg}}) = 1.9 \times 10^2 \text{ kkg 2-chlorophenol to water}$$

Atmospheric emissions were estimated to be 5%^a of the total aquatic discharge. Therefore, emissions to the air were estimated as follows:

$$(\text{total water emission}) (0.05) = (\text{total emission to air})$$

$$(1.9 \times 10^2 \text{ kkg}) (0.05) = 9.5 \text{ kkg 2-chlorophenol emitted to air}$$

2-Chlorophenol in land-destined waste materials was estimated to be negligible.

It should be noted that these emission quantities are best-guess estimates, and are subject to confirmation by monitoring data.

2.1.2.2 Minor Uses

There was no information on the use of 2-chlorophenol in the production process of phenolic resins. We estimated that in 1976, 0.5% of the total production of 2-chlorophenol was used in the production of phenolic resins; thus, the consumption of 2-chlorophenol in phenolic resin manufacturing was estimated by multiplying the total production of 2-chlorophenol by 0.5%. Therefore:

$$(9.0 \times 10^3 \text{ kkg}) (0.005) = 45 \text{ kkg 2-chlorophenol}$$

Little detailed information exists on the use of 2-chlorophenol as solvents. We estimated that in 1976, 0.5% of the total production of 2-chlorophenol was used as solvents. This corresponds to 45 kkg 2-chlorophenol (calculated as above).

2.1.2.2.1 Emissions Due to Minor Uses

There was little information on the emissions of 2-chlorophenol from minor uses. We estimated that the amount of 2-chlorophenol discharged to the environment by phenolic resin production facilities was 2% of the total consumption of 2-chlorophenol for this process. This estimate was made for calculation purposes only, and was not based on literature sources. Assuming that there was no control on the waste discharge from this process, then the emissions of 2-chlorophenol would be estimated as follows:

^a JRS estimates. See Section 3.3.3.1.1.

$$\left[\begin{array}{l} \text{total consumption} \\ \text{of 2-chlorophenol} \\ \text{for this process} \end{array} \right] (0.02) = \left[\begin{array}{l} \text{emission of} \\ \text{2-chlorophenol} \\ \text{from this process} \end{array} \right]$$

$$(45 \text{ kkg}) (0.02) = 0.9 \text{ kkg 2-chlorophenol emitted due to phenolic resin production}$$

It was reasonable to assume that most of 2-chlorophenol used as a solvent was released directly to the environment. This would amount to 45 kkg of 2-chlorophenol emitted to the environment.

It should be noted that the above estimations were not based on actual data and should be adjusted upon confirmation by monitoring or other experimental information.

2.1.3 Summary

Because of the lack of available information, many values were derived based on assumptions and estimations. These estimates should be verified in later studies to properly assess the environmental emissions of 2-chlorophenol.

Figure 2.3 shows the materials balance diagram for 2-chlorophenol.

2.2 4-CHLOROPHENOL

2.2.1 Production of 4-chlorophenol

The majority of 4-chlorophenol is produced by the direct chlorination of phenol. Hydrolysis of chlorinated benzene contributes a small quantity to the total production of 4-chlorophenol (Kirk-Othmer, 1969). Figure 2.4 shows the environmental flow diagram of 4-chlorophenol.

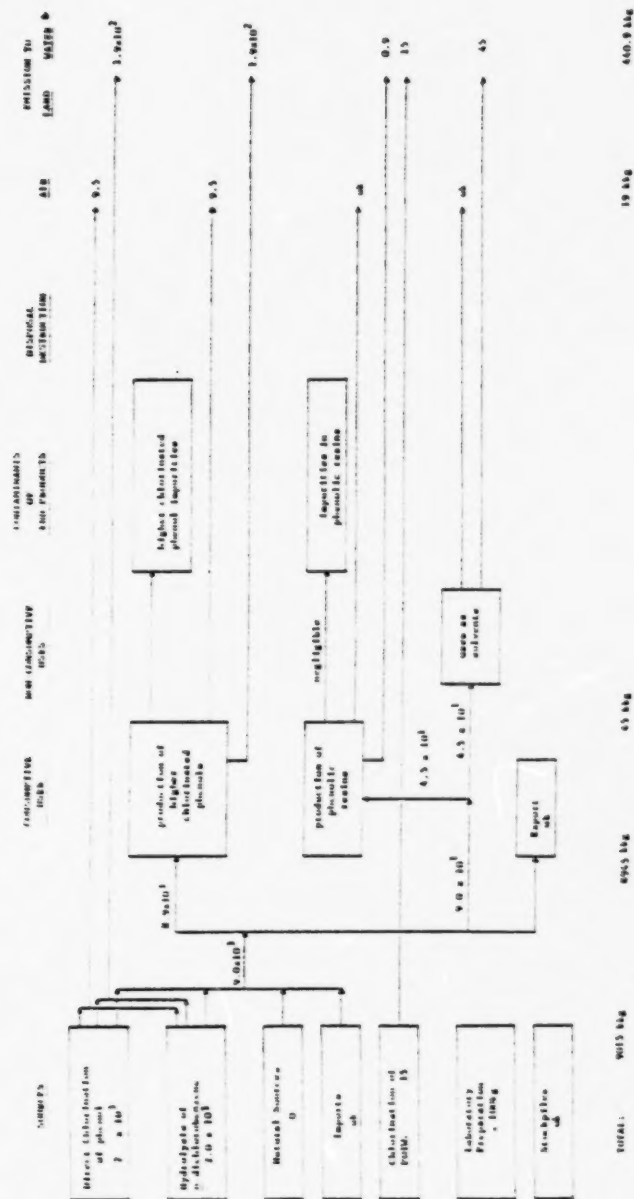
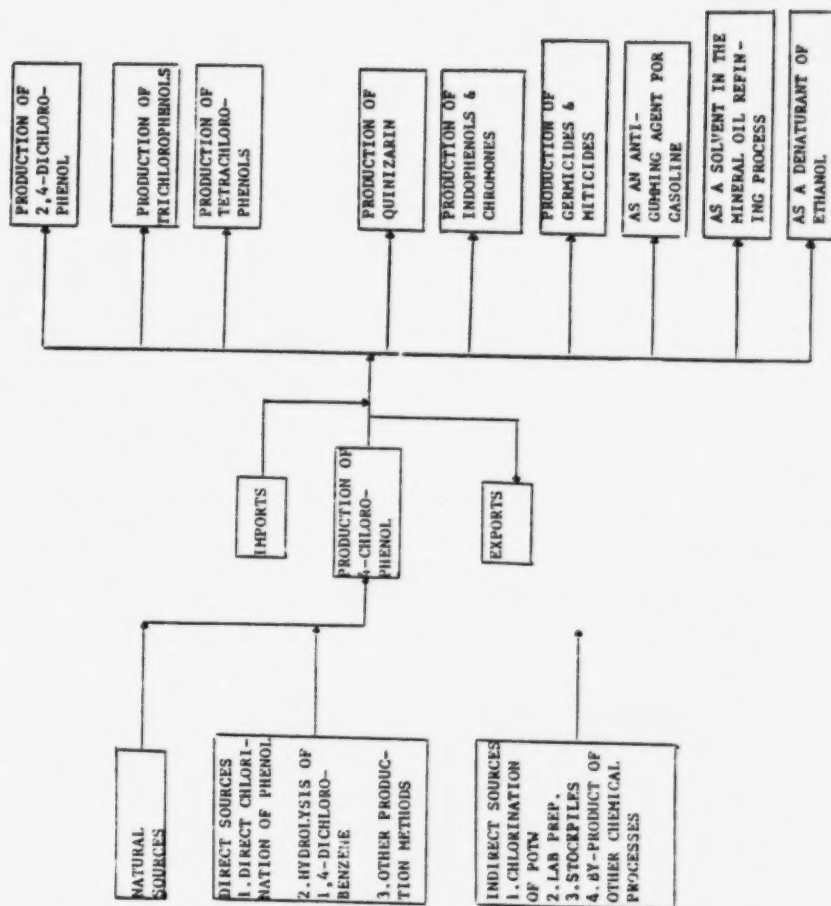


Figure 2.3 Materials Balance for 2-Chlorophenol (kg)

Reproduced from best available copy.

FIGURE 2.4 ENVIRONMENTAL FLOW DIAGRAM OF 4 - CHLOROPHENOL



2.2.1.1 Hydrolysis of p-Dichlorobenzene

The hydrolysis of p-dichlorobenzene (p-DCB) follows the same procedure described in section 2.1.1.1. The only difference is the raw material used in the production process; p-dichlorobenzene rather than o-dichlorobenzene is used to form 4-chlorophenol (Kirk-Othmer, 1969).

Stanford Research Institute has estimated that in 1976, 10% of the total production of p-dichlorobenzene was consumed in the production of 4-chlorophenol (Stanford Research Institute, 1975). The total production of p-dichlorobenzene was reported to be 1.7×10^4 kkg in 1976. Therefore the production of 4-chlorophenol (4-CP) was estimated as follows (see Section 2.1.1.1 for methods of calculation):

$$\begin{aligned} & (0.10)(1.7 \times 10^4 \text{ kkg p-DCB}) \frac{(1 \text{ kkmole p-DCB})}{(146.9 \text{ kkg p-DCB})} \frac{(0.86 \text{ kkmole 4-CP})}{(\text{kkmole p-DCB})} \times \\ & \frac{(128.5 \text{ kkg 4-CP})}{(\text{kkmole 4-CP})} = 1.3 \times 10^3 \text{ kkg of 4-chlorophenol produced by hydrolysis} \end{aligned}$$

2.2.1.2 Direct Chlorination of Phenol

As pointed out in Section 2.1.1.2 most 4-chlorophenol was produced by the direct chlorination of phenol. Yield of 4-chlorophenol was estimated at 55%^a. The quantity of 2-chlorophenol produced via the direct chlorination process was estimated at 7.0×10^3 kkg in 1976. Thus, the production of 4-chlorophenol was estimated by multiplying the quantity of 2-chlorophenol produced from phenol by the ratio 55%/45%. Therefore:

$$(7.0 \times 10^3 \text{ kkg}) \frac{(0.55)}{(0.45)} = 8.6 \times 10^3 \text{ kkg 4-chlorophenol produced by chlorination}$$

The total production of 4-chlorophenol in 1976 was then estimated by adding the production of 4-chlorophenol via the direct chlorination process to the quantity of 4-chlorophenol produced by the hydrolysis method:

$$8.6 \times 10^3 \text{ kkg} + 1.3 \times 10^3 \text{ kkg} = 9.9 \times 10^3 \text{ kkg 4-chlorophenol produced}$$

^a See Section 2.1.1.1

2.2.1.3 Chlorination by POTW

As pointed out in section 2.1.1.3, chlorination of municipal water is a potential indirect source of production of 2-chlorophenol and 4-chlorophenol. The total estimated amount of 2-chlorophenol produced by this source was 15 kkg in 1976. Assuming that the mechanism of this reaction is the same as that occurring in the direct chlorination of phenol (see section 2.1.1.2, 2.2.1.3), it was assumed that the same product ratio is obtained in this case. Thus the quantity of 4-chlorophenol can be calculated by multiplying the quantity obtained for 2-chlorophenol by the ratio 55%/45%:

$$(15 \text{ kkg}) \frac{(0.55)}{(0.45)} = 18 \text{ kkg 4-chlorophenol produced indirectly}$$

2.2.1.4 Imports

The quantity of 4-chlorophenol imported was not reported in 1976.

2.2.1.5 Other Production Sources

No information on other possible production processes such as stockpiles or laboratory preparations was available. We estimated that the quantity contributed by these sources would be small compared to the total production quantity of 4-chlorophenol.

2.2.1.6 Emissions of 4-chlorophenol from Production

Little detailed information exists on the emissions of 4-chlorophenol to the environment. Using the same reasoning previously discussed (see section 2.1.1.6), we estimated that most of 4-chlorophenol was emitted to water and the aquatic emission factor of 2.1×10^{-2} kkg/kkg of 4-CP produced was used. Therefore, by using the same calculation method we estimated the total aquatic discharge from the production of 4-chlorophenol:

$$(9.9 \times 10^3 \text{ kkg}) (2.1 \times 10^{-2} \text{ kkg/kkg}) = 2.1 \times 10^2 \text{ kkg 4-chlorophenol emitted to water}$$

Accordingly, emission to the air was estimated as in section 2.1.1.6 by multiplying the total aquatic discharge by 5%:

$$(2.1 \times 10^2 \text{ kkg}) (0.05) = 1.1 \times 10^1 \text{ kkg 4-chlorophenol emitted to air}$$

Emission to land was estimated to be negligible.

2.2.2 Uses

As shown in Figure 2.4, 4-chlorophenol was used in the production of higher chlorinated phenols, quinizarin, indophenols and chromones. It was also consumed in the production of germicides and miticides. Its salt finds use as an anti-gumming agent for gasoline. It has also been used as a solvent in the refining of mineral oil and as a denaturant of ethanol. (Kirk-Othmer, 1969).

Information on most of these production processes was not available.

2.2.2.1 Production of Higher Chlorinated Phenols

Most 4-chlorophenol produced in the United States was used for the production of 2,4-dichlorophenol (Kirk-Othmer, 1969); 2,6-dichlorophenol was not formed upon direct chlorination of 4-chlorophenol. Trichlorophenols and tetrachlorophenols were also produced by the chlorination of 4-chlorophenol.

We estimated that in 1976, 87% of the total production of 4-chlorophenol was used in the production of higher chlorinated phenols. It should be noted that this estimation was only used for calculation purposes and was not based on any literature values. The amount of 4-chlorophenol used in this production process was calculated by multiplying the total production quantity by a factor of 0.87. Therefore:

$$(9.9 \times 10^3 \text{ kkg}) (0.87) = 8.6 \times 10^3 \text{ kkg 4-chlorophenol consumed}$$

2.2.2.1.1 Emissions Due to 4-Chlorophenol Chlorination

Information on the emissions of 4-chlorophenol to the environment was not available. Using the assumptions and estimations discussed in section 3.1.2.1.1, we arrived at an aquatic emission factor of 2.1×10^{-2} kkg per kkg consumed and

estimated that emissions to air were 5% of emissions to water. Emissions to land were estimated to be negligible. The total emission of 4-chlorophenol to water was estimated by multiplying the total consumption of 4-chlorophenol for this process by the aquatic emission factor. In that case:

$$(8.6 \times 10^3 \text{ kkg}) (2.1 \times 10^{-2} \text{ kkg/kkg}) = 1.8 \times 10^2 \text{ kkg 4-chlorophenol emitted to water due to further chlorination}$$

Emissions of 4-chlorophenol to air were then estimated by multiplying the emission quantity to water by 0.05:

$$(1.8 \times 10^2 \text{ kkg}) (0.05) = 9 \text{ kkg 4-chlorophenol emitted to air due to further chlorination}$$

2.2.2.2 Production of Quinizarin

In 1976, the production of quinizarin was reported at 1,717,000 lbs. or 7.79×10^2 kkg (USITC). The production plants were American Cyanamid, Tom Rivers Corp., Tennessee Eastman Corp., Harshaw Chemical Corp., and E. I. DuPont de Nemours Co. The plant locations are shown in figure 2.5.

4-chlorophenol was used as a raw material in the production of quinizarin. The basic reactions in this process are:

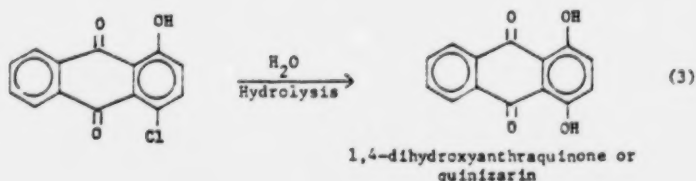
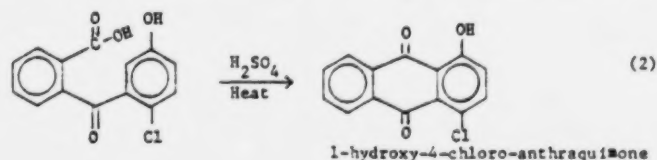
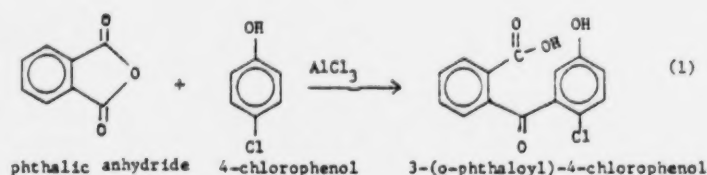
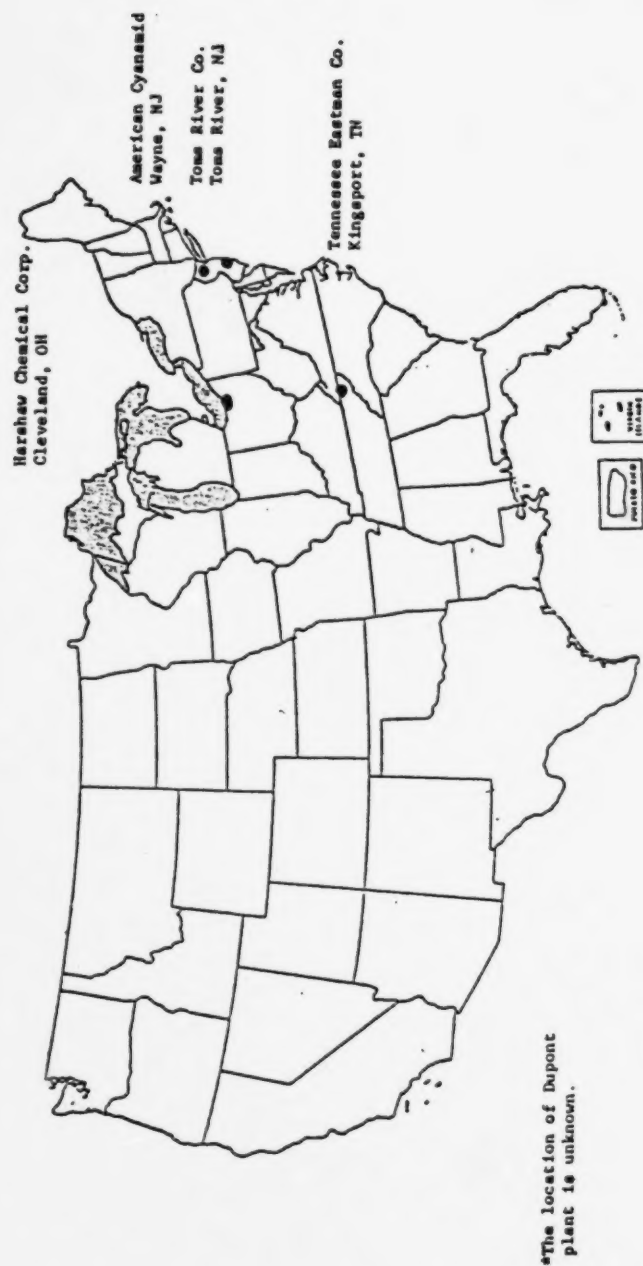


FIGURE 2.5 LOCATIONS OF QUINIZARIN PRODUCTION FACILITIES



We estimated that a 90% conversion rate would be achieved for each reaction step. This estimation was based on engineering judgements on the economic feasibility of industrial processes. The total amount of 4-chlorophenol consumed in the production of quinizarin was calculated by multiplying the following factors:

- (1) The total production of quinizarin produced in 1976.
- (2) The reciprocal of the molecular weight of quinizarin.
- (3) The reciprocal percent of theoretical yield for reaction (3)
- (4) The reciprocal percent of theoretical yield for reaction (2)
- (5) The reciprocal percent of theoretical yield for reaction (1)
- (6) The molecular weight of 4-chlorophenol.

Therefore:

$$\begin{array}{ccccccccc}
 (7.79 \times 10^2) & \left(\frac{1}{240.23} \right) & \left(\frac{1}{0.90} \right) & \left(\frac{1}{0.90} \right) & \left(\frac{1}{0.90} \right) & (128.56) & = & 5.7 \times 10^2 \text{ kkg} \\
 (1) & (2) & (3) & (4) & (5) & (6) & & \text{4-chlorophenol} \\
 & & & & & & & \text{consumed in} \\
 & & & & & & & \text{quinizarin synthesis}
 \end{array}$$

This calculated figure amounted to 5% of the total consumption of 4-chlorophenol in 1976.

2.2.2.2.1 Emissions Due to Quinizarin Synthesis

Information on emissions of 4-chlorophenol from the production of quinizarin was not available. We estimated that the amount of 4-chlorophenol contained in the end-product quinizarin would be minimal, but more information is needed to confirm this assumption.

It was estimated that emissions to water were 3% of the total consumption of 4-chlorophenol in this process, based on the water solubility of the chemical, and considering similar production processes for chemical intermediates used in dye manufactures. Therefore, the total water emissions were estimated by multiplying the amount of 4-chlorophenol consumed by this process by the emission factor.

$$(5.7 \times 10^2 \text{ kkg}) (0.03) = 1.7 \times 10^1 \text{ kkg 4-chlorophenol emitted to water}$$

Because of the low volatility of 4-chlorophenol, emissions to air were estimated to be 5% of the total aquatic emission. Emissions to air were obtained by multiplying the aquatic emission by the factor of 0.05:

$$(1.7 \times 10^1 \text{ kkg}) (0.05) = 8.5 \times 10^{-1} \text{ kkg 4-chlorophenol emitted to air}$$

The amount of 4-chlorophenol present in land-destined waste discharged by the production of quinizarin was estimated to be negligible compared to the total emission.

2.2.2.3 Production of Indophenols and Chromones

4-Chlorophenol reacts with 2-alkylacetoacetates in the presence of phosphorus pentoxide to produce chromones. Likewise, it reacts with indene hydrochloride and o-nitrobenzenesulfonic acids to produce indophenols. The produced indophenols and chromones have been used in the dye industry. (Kirk-Othmer, 1969)

Information on the production quantities and processes for these chemical intermediates was not available. We estimated that 3% of the total production of 4-chlorophenol was consumed in the production of these chemicals. Thus, the total consumption of 4-chlorophenol in these production processes was estimated by multiplying the annual production quantity by the 3% factor:

$$(9.9 \times 10^3 \text{ kkg}) (0.03) = 3.0 \times 10^2 \text{ kkg 4-chlorophenol consumed}$$

2.2.2.3.1 Emissions Due to Indophenol and Chromone Synthesis

Based on similar production processes for chemical intermediates used in the manufacturing of dyes (see section 2.2.2.2.1) we estimated that 3% of the 4-chlorophenol consumed was lost as waterborne emission from these production processes. The total aquatic emission was calculated by the general method described in section 3.2.2.2.1. In this case,

$$(3.0 \times 10^2 \text{ kkg}) (0.03) = 9.0 \text{ kkg 4-chlorophenol emitted to water}$$

The atmospheric emissions associated with this process were then estimated by multiplying the waterborne emission by a factor of 5% (see section 3.2.2.2.1). Therefore,

$$(9.0 \text{ kkg}) (0.05) = 4.5 \times 10^{-1} \text{ kkg 4-chlorophenol emitted to air}$$

As mentioned in previous estimates, emissions to land were estimated to be negligible.

Again, it should be mentioned that the above calculations and estimations do not reflect actual emission data due to lack of information on the production quantities, production processes, and emission factors.

2.2.2.4 Production of Germicides and Miticides

4-chlorophenol reacts with benzyl chloride to produce O-(4-chlorophenyl)-o-cresol, a widely used germicide. The reaction of 4-chlorophenol with p-chloro-benzenesulfonyl chloride gives p-chlorophenyl-p-chloro-benzenesulfonate, a miticide sold by Dow Chemical Company. (Kirk-Othmer, 1969). Other information pertaining to the production methods and quantities was not available.

We assumed that 2% of the total 4-chlorophenol production in 1976 was consumed in the synthesis of germicides and miticides. This assumption was made only for calculation purposes. The total consumption of 4-chlorophenol was then obtained by multiplying the total annual production of 4-chlorophenol by 2%. Therefore:

$$(9.9 \times 10^3) (0.02) = 2.0 \times 10^2 \text{ kkg 4-chlorophenol consumed in germicide and miticide synthesis}$$

2.2.2.4.1 Emissions Due to Germicide and Miticide Synthesis

Little information pertaining to the production process and quantity of germicides and miticides was available. Based on a similar pesticide synthesis process (synthesis of PCP salt, see section 6.4.4.1), we estimated the waterborne emission factor to be 1.5×10^{-3} kkg per kkg of 4-chlorophenol consumed, and the emission factor to air as 5×10^{-5} kkg/kkg consumed. The total emission

to water was estimated by multiplying the amount of 4-chlorophenol used in the production of germicides and miticides by the waterborne emission factor:

$$(2.0 \times 10^2 \text{ kkg}) (1.5 \times 10^{-3} \text{ kkg/kkg}) = 3.0 \times 10^{-1} \text{ kkg 4-chlorophenol emitted to water}$$

The emission of 4-chlorophenol to air was calculated by multiplying the annual consumption of 4-chlorophenol in this process by the airborne emission factor:

$$(2.0 \times 10^2 \text{ kkg}) (5 \times 10^{-5} \text{ kkg/kkg}) = 1.0 \times 10^{-2} \text{ kkg 4-chlorophenol emitted to air}$$

Emission to land was estimated to be negligible compared to the total emission quantity.

4-Chlorophenol may be present in the finished germicide or miticide products as a contaminant, but the amount could not be estimated and was considered negligible compared to the bulk emissions from the production facilities.

Again, these assumptions and estimations should be verified in further studies.

2.2.2.5 Use of 4-Chlorophenol as a Denaturant for Ethanol

There was no information on the amount of 4-chlorophenol used as a denaturant for ethanol (Kirk-Othmer, 1969). We estimated that in 1976, 1% of the total consumption of 4-chlorophenol was used in the denaturation of ethanol. This estimate was based on the following reasoning. In 1976, 4.0×10^5 kkg of ethanol were consumed in the United States (USITC). We estimated that 80% of the total ethanol production quantity was denatured, and the remaining 20% was 100% pure ethanol. Therefore, the estimated total denatured ethanol in 1976 was calculated by multiplying the total consumption of ethanol by a factor of 0.8:

$$(4.0 \times 10^5 \text{ kkg}) (0.8) = 3.2 \times 10^5 \text{ kkg denatured ethanol produced in 1976}$$

We then assumed that the 4-chlorophenol used as a denaturant for ethyl alcohol was present in the range of 0.01% to 0.05% (w/w) in ethanol. Therefore, an average of 0.03 weight % of 4-chlorophenol was assumed to be contained in the denatured ethanol. The estimated amount of 4-chlorophenol used as a denaturant for ethanol can then be calculated by multiplying the total denatured ethanol consumption by a factor of 0.03%:

$$(3.2 \times 10^5 \text{ kkg}) (0.0003) = 9.6 \times 10^1 \text{ kkg 4-chlorophenol used for ethanol denaturation}$$

This figure would then amount to approximately 1% of the total consumption of 4-chlorophenol (9.9×10^3 kkg).

2.2.2.5.1 Emissions Due to Use as a Denaturant for Ethanol

4-Chlorophenol is readily soluble in ethanol. Thus, we assumed that all the 4-chlorophenol used as a denaturant of ethanol would be released to the environment by the dispersive uses of ethyl alcohol. Therefore, the total emissions of 4-chlorophenol from this use amounted to 9.6×10^1 kkg in 1976.

2.2.2.6 Miscellaneous Uses of 4-Chlorophenol

Besides the above uses, 4-chlorophenol has also been used as a solvent in the refining of mineral oil, and its salts (sodium and potassium 4-chlorophenate) have been used as antigumming agents for gasoline and wash liquids for fuel gas purification (Kirk-Othmer, 1969). Information on these miscellaneous uses was not available. We estimated that the remaining 2% of the total production of 4-chlorophenol was consumed by these uses. This quantity can be calculated by multiplying the total consumption of 4-chlorophenol by a factor of 0.02:

$$(9.9 \times 10^3 \text{ kkg}) (0.02) = 2.0 \times 10^2 \text{ kkg 4-chlorophenol for miscellaneous uses}$$

2.2.2.6.1 Emissions Due to Miscellaneous Uses

We estimated that the emission of 4-chlorophenol to the environment attributed to miscellaneous uses was 60% of the amount consumed for these uses. This estimate was based on the following: 1) the use as a solvent would all

be released to the environment; 2) a small amount was released during the formulation of the antigumming agents. This percentage did not represent the exact emission quantity released from these uses, but it served as a basis for calculation purposes.

The total emissions to the environment were calculated by multiplying the total quantity of 4-chlorophenol consumed by these miscellaneous uses by the 60% factor:

$$(2.0 \times 10^2 \text{ kkg}) (0.6) = 1.2 \times 10^2 \text{ kkg 4-chlorophenol emitted due to miscellaneous uses}$$

2.2.3 Summary

Table 2.1 shows a summary of the estimated breakdown of 4-chlorophenol uses in 1976 and the quantity of 4-chlorophenol consumed by each of these categories.

Figure 2.6 shows the materials balance diagram for 4-chlorophenol.

Table 2.1 USES OF 4-CHLOROPHENOL (1976)

Type of Uses	Percentage of the total consumption of 4-chlorophenol	Quantity of 4-chlorophenol consumed (kkg)
Production of higher chlorinated phenols	87% ^a	8.6×10^3 ^a
Production of quinizarin	5%	5.7×10^2
Production of indo-phenols & chromones	3% ^a	3.0×10^2 ^a
Production of germicides and miticides	2% ^a	2.0×10^2 ^a
As a denaturant for ethanol	1% ^a	9.6×10^1 ^a
Miscellaneous uses	2% ^a	2.0×10^2 ^a
Total	100%	9.9×10^3

^a JRB estimate



2-26

3.0 2,4-DICHLOROPHENOL

This chapter presents the information available on the major dichlorophenol: 2,4-dichlorophenol (2,4-DCP). The environmental flow diagram is presented first, followed by a discussion of how the values were obtained.

3.1 FLOW DIAGRAM FOR 2,4-DICHLOROPHENOL

Figure 3.1 shows the flow diagram for 2,4-DCP, summarizing sources, uses, and emissions during the year 1976.

3.2 DIRECT PRODUCTION OF 2,4-DICHLOROPHENOL

3.2.1 Amounts Produced

No precise data on yearly production of 2,4-DCP were available. USITC did not publish data because this would reveal relative market positions of the two large and one small producers. Therefore, we had to estimate the amount of 2,4-DCP produced. Our best estimate was 39,000 kkg for the year 1976 (the year chosen for the overall materials balance). This result was obtained by selecting one of the three estimates obtained by different methods, as shown below and on Table 3.1.

The first estimate was by Tracor-Jitco, Inc. (1977a). Based on USITC data for production of other chlorophenols, they estimated 1976 production of 2,4-DCP to be 14,000 kkg. This must be a minimum estimate for two reasons: 1) Tracor-Jitco (1977a) pointed out a result by EPA (1973) estimating the 2,4-DCP production capacities of Dow and Monsanto as 4550 - 6150 kkg and 10,250 - 13,550 kkg, respectively. The sum of the low ends of the ranges is 14,800 kkg -- somewhat higher than Tracor-Jitco's estimate. 2) Tracor-Jitco (1977a) stated that only Dow and Monsanto made 2,4-DCP in 1976, whereas USITC listed Rhodia as a producer in 1976 also. Because of these uncertainties, and the lack of documentation for Tracor-Jitco's estimate, a second approach was sought.

TABLE 3.1 PRODUCTION AND SALES OF 2,4-DICHLOROPHENOL (kkg)¹

PRODUCER ⁵	1977		1976		1970	
	PRODUCTION	SALES	PRODUCTION	SALES	PRODUCTION	SALES
Dow Chemical Midland, MI			39,000 ⁴			
Monsanto Sauget, IL		4,031 ⁶	14,000 ⁷	1,911 ⁶	36,735 ³	19,762 ⁶
Rhodia Freeport, TX			14,800 - 19,800 ²			
Transvaal Jacksonville, AR						

1 Phone conversation with USITC revealed that production numbers were not publishable for any year because there were only three manufacturers (Dow, Monsanto, Rhodia) and the third was so small as to permit the others to estimate the competitor's share of the market.

2 This is the range of capacities presented in Tracor-Jitco (1977a) and attributed to an estimate by EPA (1973).

3 Value from EPA (1975a), estimated from the amount of 2,4-D produced. The 2,4-D production and basis for the estimate were not stated, so the accuracy of the number cannot be evaluated.

4 Derived from estimation of 2,4-D production as described in Section 3.2.1.

5 Stanford Research Institute, 1975 and 1978.

6 USITC, 1960 - 1978.

7 Tracor-Jitco, 1977a.

A second way to estimate production of 2,4-DCP was to assume that the manufacture of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) consumed a fixed proportion of 2,4-DCP produced each year. This method was used by EPA (1975a) and the fraction that related annual United States production of 2,4-D with their estimated 2,4-DCP production for the same year was 0.48 - 0.54, depending on the year. The 0.54 ratio for 2,4-D / 2,4-DCP was used in low production, low-demand years. When production and demand for 2,4-D increased in the late 1960s due to military use, EPA (1975a) used the 0.48 ratio (apparently assuming a larger contribution from imports). The bases for these numbers were unstated, but the values were consistent with 2,4-D being the major use of 2,4-DCP (Tracor-Jitco, 1977a).

When the 0.54 ratio was used for 2,4-D / 2,4-DCP production, we obtained a production estimate of 39,000 kkg 2,4-DCP produced in 1976 (justifying the use of the low-production ratio; production in a high-demand year like 1968 was estimated to be 78,000 kkg). This result was based on a 2,4-D production of 21,000 kkg, which was derived as follows: 1) Total production of phenoxyacetic acid herbicides in 1976 was "approximately 60 million pounds" (USITC, 1977, p. 264). We interpreted this to mean $\pm 10\%$. 2) Of these 27,000 kkg, approximately 6,000 kkg were due to 2,4,5-T production (see Chapter 4). 3) Therefore, 2,4-D derivatives must account for the remainder: 21,000 kkg with an uncertainty of $\pm 20\%$. Thus, 2,4-DCP production was:

$$(21,000 \text{ kkg } 2,4\text{-D}) \div 0.54 = 39,000 \text{ kkg } 2,4\text{-DCP in 1976}$$

A third value for production was the sum of the capacities of the two major producers. Tracor-Jitco (1977a) attributed to EPA (1973) an estimate that the annual capacities of Dow and Monsanto were 4550 - 6150 kkg and 10,250 - 13,650 kkg, respectively. The sum was 14,800 - 19,800 kkg/yr.

In estimating the 1976 production of 2,4-DCP, we had three independently-derived values: 14,000 kkg; 14,800 - 19,800 kkg; and 39,000 kkg. We used the estimate of 39,000 kkg 2,4-DCP produced in 1976 for the following two reasons: 1) It was based most directly on USITC reports; and 2) it gave a worst-case estimate when used to calculate emissions.

Four methods of synthesizing 2,4-DCP are available to industry. These are: 1) chlorination of phenol with Cl_2 ; 2) chlorination of monochlorophenols with Cl_2 ; 3) chlorination of phenol with N,N'-dichlorourea; and 4) chlorination of phenols with SO_2Cl_2 . According to EPA (1976a), the predominant process for synthesis of chlorophenols was the direct chlorination of phenol or chlorophenol with Cl_2 . To derive an estimate of the amounts of 2,4-DCP produced by chlorination of the respective feedstocks, it was assumed that chlorophenol would have more economic value as a product than as a feedstock. Therefore, it was estimated that overall 80% of the feedstock would be phenol and 20% would be chlorophenol. This proportion was then used to calculate our estimates of the amounts produced by each process:

$$\begin{aligned}(0.80) (39,000 \text{ kkg}) &= 31,200 \text{ kkg by direct chlorination of phenol} \\ (0.20) (39,000 \text{ kkg}) &= 7,800 \text{ kkg by direct chlorination of chlorophenol}\end{aligned}$$

(Since the same emission factors were applied to the two processes in calculations of releases to the environment, altering the proportions of the two processes would only change the distribution of emissions between the processes and not the total emissions.)

3.2.2 Amounts Imported

The amount of 2,4-DCP imported was not regularly reported by the USITC. Tracor-Jitco (1977a) cited a personal communication with USITC as the source of an import value for 1975: 30.5 kkg. In the absence of other data, we assumed that 30.5 kkg of 2,4-DCP were imported in 1976.

3.3 EMISSIONS DUE TO PRODUCTION AND IMPORTS

3.3.1 Emissions Due to Production

Direct data on emissions to air, land, or water during the production of 2,4-DCP were not in the readily available literature. Similarly, emission factors and monitoring data from which to calculate them were unavailable. We were able to estimate emissions based on our best judgement estimates of emission factors for each production process. Emissions were then calculated by the operation: (production in kkg) x (emission factor in kkg released / kkg produced).

The estimates of the emission factors for air, land, and water during 2,4-DCP production were based on the process flow diagram in Figure 1.1 (Tracor-Jitco, 1977a). We assumed that the diagram applied to both the Dow and Monsanto processes (the two major producers), although it was probably based on published descriptions of the Dow facility in Midland, Michigan (Sittig, 1974).

3.3.1.1 Chlorination of Phenol

3.3.1.1.1 Emissions to Air

2,4-DCP may be released to the air at the following points during its manufacture by the phenol chlorination process (see Figure 1.1): the reactor vent, the prill tower vent, the dryer vent, and the incineration of sludge (discussed later). We estimated that 31 kkg/year of 2,4-DCP were released to the air during this process in 1976. In the absence of data on emission factors to the air during chlorination of phenol, our estimate was derived from an estimated emission factor of 1×10^{-3} kkg/kkg product, within an order of magnitude. This value was based on the following: 1) Each vent is preceded by a scrubber (estimated efficiency, 95%). 2) 2,4-DCP has a relatively low vapor pressure (Chapter 1). 3) Leaks and breakdowns make a negligible contribution over the course of a year. Emissions were then calculated as follows:

$$(31,200 \text{ kkg}) \times (1 \times 10^{-3} \text{ kkg/kkg}) = 31 \text{ kkg released to air}$$

3.3.1.1.2 Emissions to Water

2,4-DCP may be released to the water at the following points during its manufacture by the phenol chlorination process: scrubber water, separator. We estimated that 665 kkg/year of 2,4-DCP were released to the water during this process in 1976. In the absence of monitoring data on 2,4-DCP production waste streams, our estimate was derived from an estimated emission factor of 2.1×10^{-2} kkg/kkg product. This value was based on the following: 1) 2,4-DCP comes in contact with a large liquid volume during its synthesis. 2) It is sparingly soluble in water (Chapter 1). 3) It is very difficult to remove all phenols from aqueous waste streams. 4) Data on the Dow plant were relevant to the other producer, Monsanto. 5) The efficiency of the water treatment process used by Dow (trickling filter plus activated sludge treatment) was 86%, as reported for pilot plant

studies on this sequence (Tracor-Jitco, 1977a). 6) 85% of the synthesized 2,4-DCP was isolated; the rest entered the waste water stream. 7) 86% of this 2,4-DCP was removed by water treatment before release from the plant. The overall emission factor, then, was:

$$(0.15)(0.14) = 2.1 \times 10^{-2} \text{ kkg/kg product, or 2.1\% release.}$$

The uncertainty of this factor was estimated to be +10%, -30%.

Emissions were then calculated as follows:

$$(31,200 \text{ kkg}) \times (2.1 \times 10^{-2} \text{ kkg/kg}) = 655 \text{ kkg/year 2,4-DCP released to water}$$

This emission was a near-maximum estimate because 1) the production value, 31,200 kkg/yr, was a maximum value; and 2) the emission factor was more likely to be too high (if efficiencies and recoveries were better than estimated) than too low. The uncertainty in the emissions to water was estimated to be +10%, -70%

3.3.1.1.3 Emissions to Air Due to Incineration of Solid Residues

Solid residues containing 2,4-DCP can be formed at the following points in the phenol chlorination process: still residues, sludge from wastewater treatment, ash from incinerator. We estimated that 0.2 kkg of 2,4-DCP was released to the air due to treatment of this solid residue in 1976. Releases to water and land were estimated to be zero. In the absence of monitoring data on incinerator plumes, our estimate was derived from an emission factor of 2.5×10^{-6} kkg/kg product for reactor tars and 3.2×10^{-6} kkg/kg product for biological treatment sludge. Disposal of incineration ash was estimated to produce no emissions of 2,4-DCP.

The emission factor for disposal of reactor tars was estimated based on the following: 1) Reactor tars were estimated to contain 1×10^{-3} kkg 2,4-DCP/kg product, because it would be economically advantageous to extract the 2,4-DCP from the tar if it amounted to as much as 1-5% of the product yield. 2) Incineration of this tar (1000°C) (Sittig, 1974) was 95% efficient. 3) Capture of released 2,4-DCP by the incinerator scrubber (Sittig, 1974) was 95% efficient. The emission factor for tar incineration was calculated as:

$$(0.05) \times (0.05) \times (1 \times 10^{-3}) = 2.5 \times 10^{-6} \text{ kkg 2,4-DCP released/kg product}$$

The releases to air due to incineration of reactor tars were then calculated by the process:

$$(31,200 \text{ kkg}) \times (2.5 \times 10^{-6} \text{ kkg/kkg product}) = 0.1 \text{ kkg/year 2,4-DCP emitted to the atmosphere due to reactor tar incineration}$$

We estimated the uncertainty of this value as +100%, - 50%.

The emission factor for disposal of biological treatment sludge was estimated based on the following: 1) 15% of 2,4-DCP synthesized entered the water waste stream. 2) Of this, 86% was removed by the trickling filter/activated sludge sequence (Tracor-Jitco, 1977a). 3) Since 2,4-DCP is degradable by acclimated sludge (EPA, 1975a), we estimated that only 1% of aqueous 2,4-DCP was carried over unchanged into the sludge. 4) Incineration of this sludge (1000°C) (Sittig, 1974) was 95% efficient. 5) Capture of released 2,4-DCP by the incineration scrubber (Sittig, 1974) was 95% efficient. The emission factor for sludge incineration was calculated as:

$$(0.15) \times (0.86) \times (0.01) \times (0.05) \times (0.05) = 3.2 \times 10^{-6} \text{ kkg/kkg product}$$

The releases to air due to disposal of biological treatment sludge were then calculated to be:

$$(31,200 \text{ kkg}) \times (3.2 \times 10^{-6} \text{ kkg/kkg product}) = 0.1 \text{ kkg/year 2,4-DCP emitted to the atmosphere due to disposal of biological treatment sludge}$$

We estimated the uncertainty of this number as +500%, - 95% (mostly due to the estimate of the amount of 2,4-DCP carried unchanged into the sludge).

The sum of air emissions due to solid residue disposal was then estimated to be $0.1 \text{ kkg} + 0.1 \text{ kkg} = 0.2 \text{ kkg/year}$.

3.3.1.1.4 Emissions to Land

It was estimated that disposal of incinerator ash produced zero emissions of 2,4-DCP. There was no mention in the literature (Sittig, 1974) of direct application of 2,4-DCP - containing wastes to land.

3.3.1.2 Chlorination of Monochlorophenols

3.3.1.2.1 Emissions to Air

2,4-DCP may be released to the air at the following points during its manufacture by the chlorophenol chlorination process (see Figure 1.1): the reactor vent, the prill tower vent, the dryer vent, and the incineration of sludge (discussed later). We estimated that 8 kkg of 2,4-DCP were released to the air during this process in 1976. In the absence of data on emission factors to the air during chlorination of chlorophenol, our estimate was derived from an estimated emission factor of 1×10^{-3} kkg/kkg product, within an order of magnitude. This value was based on the following: 1) Each vent was preceded by a scrubber (estimated efficiency, 95%). 2) 2,4-DCP has a relatively low vapor pressure (Chapter 1). 3) Leaks and breakdowns made a negligible contribution over the course of a year. Emissions were then calculated as follows:

$$(7,800 \text{ kkg}) \times (1 \times 10^{-3} \text{ kkg/kkg}) = 8 \text{ kkg released to air}$$

3.3.1.2.2 Emissions to Water

2,4-DCP may be released to the water at the following points during its manufacture by the chlorophenol chlorination process (see Figure 1.1): scrubber water, separator. We estimated that 164 kkg of 2,4-DCP were released to the water during this process in 1976. In the absence of monitoring data on 2,4-DCP production waste streams, our estimate was derived from an estimated emission factor of 2.1×10^{-2} kkg/kkg product. This value was based on the following: 1) 2,4-DCP came in contact with a large liquid volume during its synthesis, 2) It is sparingly soluble in water (Chapter 1). 3) It was very difficult to remove all phenols from aqueous waste streams. 4) Data on the Dow plant were relevant to the other producer, Monsanto. 5) The efficiency of the water treatment process used by Dow (trickling filter plus activated sludge treatment) was 86%, as reported for pilot plant studies on this sequence (Tracor-Jitco, 1977a). 6) 85% of the synthesized 2,4-DCP was isolated; the rest entered the waste water stream. 7) 86% of this 2,4-DCP was removed by water treatment before release from the plant. The overall emission factor, then is:

$$(0.15) (0.14) = 2.1 \times 10^{-2} \text{ kkg/kkg product, or 2.1\% release}$$

Emissions were then calculated as follows:

$$(7,800 \text{ kkg}) \times (2.1 \times 10^{-2} \text{ kkg/kkg}) = 164 \text{ kkg/year 2,4-DCP released to water}$$

This emission was a near-maximum estimate because 1) the 1976 production value, 7,800 kkg, was a maximum value; and 2) the emission factor was more likely to be too high (if efficiencies and recoveries were better than estimated) than too low. The uncertainty in the emissions to water was estimated to be +10%, -70%.

3.3.1.2.3 Emissions to Air Due to Incineration of Solid Residues

Solid residues containing 2,4-DCP can be formed at the following points in the chlorophenol chlorination process (see Figure 1.1): still residues, sludge from wastewater treatment, ash from incinerator. We estimated that 0.0 kkg of 2,4-DCP was released to the air due to treatment of this solid residue in 1976. Releases to waste water and land were estimated to be zero. In the absence of monitoring data on incinerator plumes, our estimate was derived from an emission factor of 2.5×10^{-6} kkg/kkg product for reactor tars and 3.2×10^{-6} kkg/kkg product for biological treatment sludge. Disposal of incinerator ash was estimated to produce no emissions of 2,4-DCP.

The emission factor for disposal of reactor tars was estimated based on the following: 1) Reactor tars were estimated to contain 1×10^{-3} kkg 2,4-DCP/kkg product, because it would be economically advantageous to extract the 2,4-DCP from the tar if it amounted to as much as 1-5% of the product yield. 2) Incineration of this tar (1000°C) (Sittig, 1974) was 95% efficient. 3) Capture of released 2,4-DCP by the incinerator scrubber (Sittig, 1974) was 95% efficient. The emission factor for tar incineration was calculated as:

$$(0.05) \times (0.05) \times (1 \times 10^{-3}) = 2.5 \times 10^{-6} \text{ kkg 2,4-DCP released/kkg product}$$

The releases to air due to incineration of reactor tars were then calculated by the process:

$$(7,800 \text{ kkg}) \times (2.5 \times 10^{-6} \text{ kkg/kkg product}) = 0.02 \text{ kkg/year 2,4-DCP}$$

emitted to the atmosphere due
to reactor tar incineration

We estimated the uncertainty of this value as +100%, -50%.

The emission factor for disposal of biological treatment sludge was estimated based on the following: 1) 15% of 2,4-DCP synthesized entered the water waste stream. 2) Of this, 86% was removed by the trickling filter/activated sludge sequence (Tracor-Jitco, 1977a). 3) Since 2,4-DCP is degradable by acclimated sludge (EPA, 1975), we estimated that only 1% of aqueous 2,4-DCP was carried over unchanged into the sludge. 4) Incineration of this sludge (1000°C) (Sittig, 1974) was 95% efficient. 5) Capture of released 2,4-DCP by the incineration scrubber (Sittig, 1974) was 95% efficient. The emission factor for sludge incineration was calculated as:

$$(0.15) \times (0.86) \times (0.01) \times (0.05) \times (0.05) = 3.2 \times 10^{-6} \text{ kkg/kkg product}$$

The releases to air due to disposal of biological treatment sludge were then calculated to be:

$$(7,800 \text{ kkg}) \times (3.2 \times 10^{-6} \text{ kkg/kkg product}) = 0.02 \text{ kkg/year 2,4-DCP emitted to the atmosphere due to disposal of biological treatment sludge}$$

We estimated the uncertainty of this number as +500%, -95% (mostly due to the estimate of the amount of 2,4-DCP carried unchanged into the sludge).

The sum of air emissions due to solid residue disposal was then estimated to be $0.02 \text{ kkg} + 0.02 \text{ kkg} = 0.04 \text{ kkg/year}$.

3.3.1.2.4 Emissions to Land

It was estimated that disposal of incinerator ash produced zero emissions of 2,4-DCP. There was no mention in the literature (Sittig, 1974) of direct application of 2,4-DCP containing wastes to land.

3.3.2 Emission Due to Imports

We estimate that the transport and storage of imported 2,4-DCP would make a negligible contribution to total air, land, and water emissions. This was based on the following: 1) Imports of 2,4-DCP (Section 3.2.2) were only 31 kkg in 1976 -- a very small fraction of production (0.08%); 2) The emission factor for a process analogous to the storage of 2,4-DCP -- the storage of aniline -- is about $4 \times 10^{-6} \text{ kkg/kkg stored}$ (Hydroscience, Inc., 1979). The calculated emission to air would be 0.001 kkg/year due to storage.

3.3.3 Emissions Due to Other Sources of Production

3.3.3.1 Emissions Due to Chlorination of Phenol-Containing Water

Phenol is easily chlorinated by dissolved Cl_2 , and chlorophenols are formed by chlorinating phenol-containing waste waters or drinking water supplied (Tracor-Jitco, 1977a; EPA, 1977). We estimated the amount of 2,4-DCP produced in drinking water by chlorination of phenol to be 8.2 kkg in 1976. This estimate was based on the following: 1) The National Organics Monitoring Survey (EPA, 1977) reported that the average 2,4-DCP concentration in 56 drinking water samples containing the compound was 0.18 ppb; 2) The daily usage of water in the U.S. was 148 gal/day/person (Metcalf and Eddy, 1972); 3) In order to give a maximum estimate, we assumed that the entire water supply contained 0.2 ppb 2,4-DCP. Actually only 56 out of 117 samples contained 2,4-DCP. The amount of 2,4-DCP present was estimated to be:

$$(148 \text{ gal/day/person}) \times (2 \times 10^8 \text{ people}) \times (3.791 \text{ kg/gal}) \times (10^{-3} \text{ kkg/kg}) \times (365 \text{ day/year}) \times (0.2 \times 10^{-9}) = 8.2 \text{ kkg 2,4-DCP present per year}$$

This was a maximum estimate because: 1) There were phenol-free water supplies in the U.S.; 2) An unknown amount of the 2,4-DCP was already present in the intake water.

3.4 EMISSIONS DUE TO CONSUMPTION AND USE

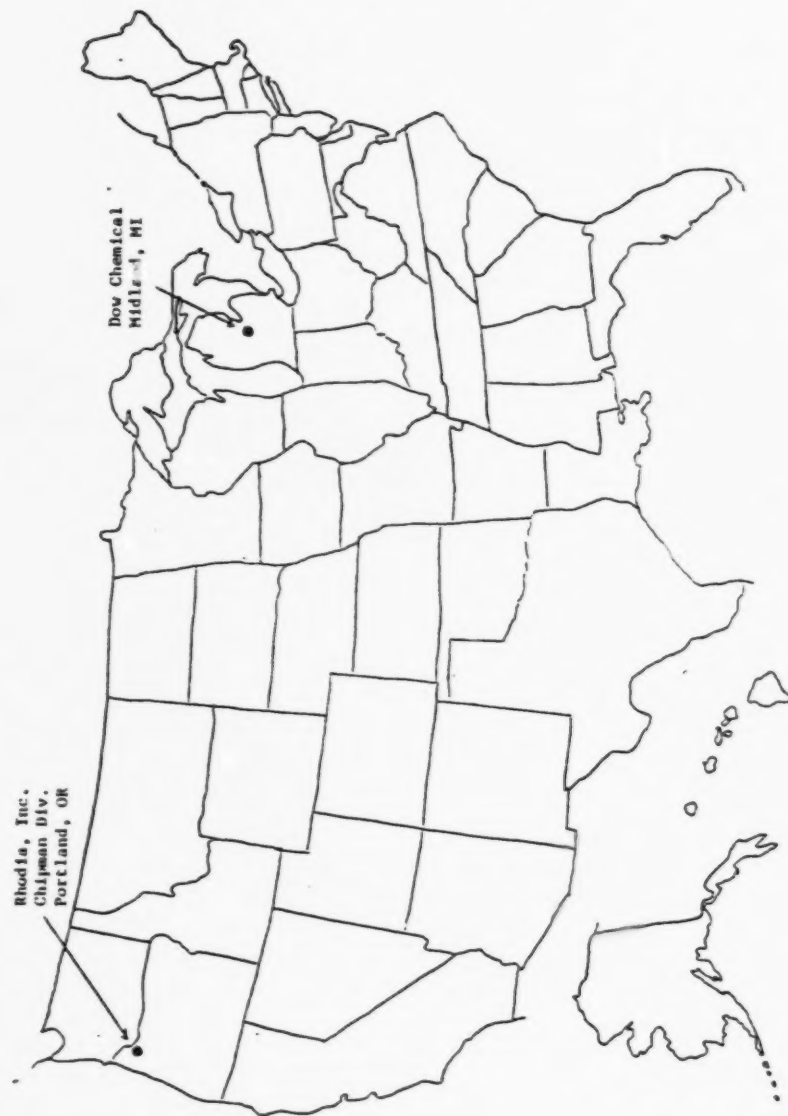
3.4.1 2,4-Dichlorophenoxyacetic Acid (2,4-D) Manufacture

According to Tracor-Jitco (1977a), and EPA (1975a) the major use of 2,4-DCP in 1976 was the synthesis of the herbicide 2,4-D.

3.4.1.1 Producers of 2,4-D

Figure 3.2 shows the names and locations of the firms listed as 1976 producers of 2,4-D by USITC (1977). Producers of 2,4-D are to be distinguished from formulators of commercial products containing 2,4-D, who purchase starting materials and do not synthesize them. There were approximately 240 formulators listed by PEDCo Environmental (1979), and the number of formulations produced for sale was in the hundreds.

FIGURE 3.2 PRODUCERS AND PRODUCTION SITES FOR 2,4-D



3.4.1.2 Amounts of 2,4-D Produced

No comprehensive data were available on 2,4-D production, and production figures for individual companies were proprietary. Therefore, we made an estimate of 2,4-D production by using other data from USITC (1977). It was estimated that 21,000 kkg of 2,4-D were produced in 1976. The selection of this value was based on the following: USITC (1977) data show a production of 2,4-D isooctylester and dimethylamine salt totaling 10,900 kkg. Other derivatives were not included in this total, so it was a minimum. We estimated 2,4-D production by another method (described in section 3.2.1) and obtained 21,000 kkg as the 1976 production of 2,4-D. We have used this latter value in further calculations for the following reasons: 1) We know that the actual production was greater than just the sum of two derivatives; and 2) less uncertainty was involved in calculating the 21,000 kkg value (section 3.2.1).

Of the producers of 2,4-D listed in Figure 3.2, Dow was credited with 90% of the market with Rhodia holding the other 10% (EPA, 1976b). It appeared that Transvaal stopped making 2,4-D between 1973 and 1976. Transvaal was a producer before 1973, according to Ottinger *et al.* (1973), but neither USITC (1977) nor EPA (1976a) listed Transvaal as a producer in 1976. Consequently, it is absent from Figure 3.3.

By applying the market percentages given above to the total 2,4-D production, the 1976 production attributable to the two producers would be: Dow, 18,900 kkg; Rhodia, 2,100 kkg.

3.4.1.3 Emissions Due to 2,4-D Synthesis

3.4.1.3.1 Emissions to the Air

2,4-DCP can be released to the air by venting during 2,4-D synthesis. We estimated that 2.1 kkg of 2,4-DCP were emitted to the air during this process in 1976. In the absence of direct data on emissions or emission factors to the air, we estimated an emission factor of 1×10^{-4} kkg 2,4-DCP emitted/kkg 2,4-D produced. The basis for this estimate was as follows: 1) We assumed that the production processes for 2,4-D synthesis are generally similar to those of 2,4-DCP synthesis.

2) We noted that Dow Chemical, the major producer, synthesized 2,4-D at its Midland, MI, plant; therefore, the emission control characteristics considered for 2,4-DCP synthesis also applied to 2,4-D synthesis. 3) In section 3.1.1.1 we estimated the emission factor for release of 2,4-DCP to air during 2,4-DCP production to be 1×10^{-3} kkg/kg product. 4) The emission factor should have been about one order of magnitude smaller for 2,4-D synthesis, because (a) most of the 2,4-DCP was consumed in the first step of the process, and (b) unreacted 2,4-DCP was captured and recycled. We therefore estimated that an emission factor of 1×10^{-4} kkg/kg 2,4-D produced was appropriate within an order of magnitude. Application of this emission factor to the synthesis of 2,4-D yielded:

$$(21,000 \text{ kkg } 2,4\text{-D}) \times (1 \times 10^{-4} \text{ kkg/kg } 2,4\text{-D}) = 2.1 \text{ kkg } 2,4\text{-DCP released to the air due to } 2,4\text{-D synthesis in 1976}$$

3.4.1.3.2 Emissions to Water

No direct information was available on amounts of 2,4-DCP released to water during 2,4-D synthesis. However, published emission factors for waste streams from anonymous plants producing 2,4-D permitted calculation of 2,4-DCP releases to water. The amount released to water was estimated to be 42 kkg/year. This emission was based on an emission factor of 2.01×10^{-3} kkg/kg product, which was estimated as follows: 1) EPA published monitoring data for two anonymous plants producing 2,4-D, and presented the results as emission factors for phenols (assumed: total phenols) in the waste streams. The values were: 1.61 kg phenols/kg 2,4-D product (a daily average); 2.75 kg/kg (a daily composite) and 1.67 kg/kg (a plant-supplied estimate). 2) We had no reason a priori to discard any of the values. 3) Therefore, we used the average of these values. 4) In using this average, we were assuming that all "phenol" was 2,4-DCP. The emission factor was therefore a maximum value. The emission factor for release of 2,4-DCP to water during 2,4-D synthesis was 2.01×10^{-3} kkg/kg product. Emissions were obtained by the operation:

$$(21,000 \text{ kkg produced}) \times (2.01 \times 10^{-3} \text{ kkg/kg}) = 42 \text{ kkg } 2,4\text{-DCP released to water due to } 2,4\text{-D synthesis in 1976}$$

The uncertainty of the emission factor was estimated to be +5%, - 90% (since it was a maximum). The production value for 2,4-D was a maximum value also. Therefore, the amount of emissions (42 kkg/year) was a maximum, and had an estimated uncertainty of +5%, - 95%.

3.4.1.3.3 Emissions Due to Disposal of Solid Residues

Direct data were not available on emissions due to disposal of solid residues from 2,4-D production. These residues would be formed as reactor tars, and as biological waste water treatment sludge. We estimated the total release to air due to incineration of solids containing 2,4-DCP to be 0.1 kkg 2,4-DCP in 1976. This estimate was based on the following: 1) We assumed the efficiencies estimated in section 3.3.1.1.3 for disposal of solid residues during 2,4-DCP production were valid for 2,4-D production in the same or a similar plant. 2) The only modification was that there would be less 2,4-DCP in the sludge because 2,4-DCP was consumed in the first step of the process. 3) The overall emission factor for reactor tar would be the same as for 2,4-DCP synthesis: 2.5×10^{-6} kkg/kg product. 4) The emission factor for biological treatment sludge would be 5-fold lower: $(3.2 \times 10^{-6} \text{ kkg/kg product}) \times (0.2) = 6.4 \times 10^{-7}$ kkg/kg product. Applying these emission factors to 2,4-D synthesis yielded the emission amounts:

$$(2.5 \times 10^{-6} \text{ kkg/kg product}) \times (21,000 \text{ kkg}) = 0.05 \text{ kkg from tars}$$

$$(6.4 \times 10^{-7} \text{ kkg/kg}) \times (21,000 \text{ kkg}) = 0.01 \text{ kkg from sludge}$$

The sum was 0.06 kkg of 2,4-DCP released to air due to disposal of solid residues. This is entered on Figures 3.1 and 3.3 as 0.1 kkg.

3.4.2 Timber Processing

Versar (1977b) reported a value for total emissions of 2,4-DCP to water by the timber processing industry in 1976. The estimate was 4 kkg (gross annual discharge). We had no way to evaluate the accuracy of this estimate.

3.4.3 Leather Tanning and Finishing

Versar (1977b) reported a value for total emissions of 2,4-DCP to water by the leather tanning and finishing industry. The estimate was 0.1 kkg (gross annual discharge). We had no way to evaluate the accuracy of this estimate.

3.4.4 Impurities in 2,4-D

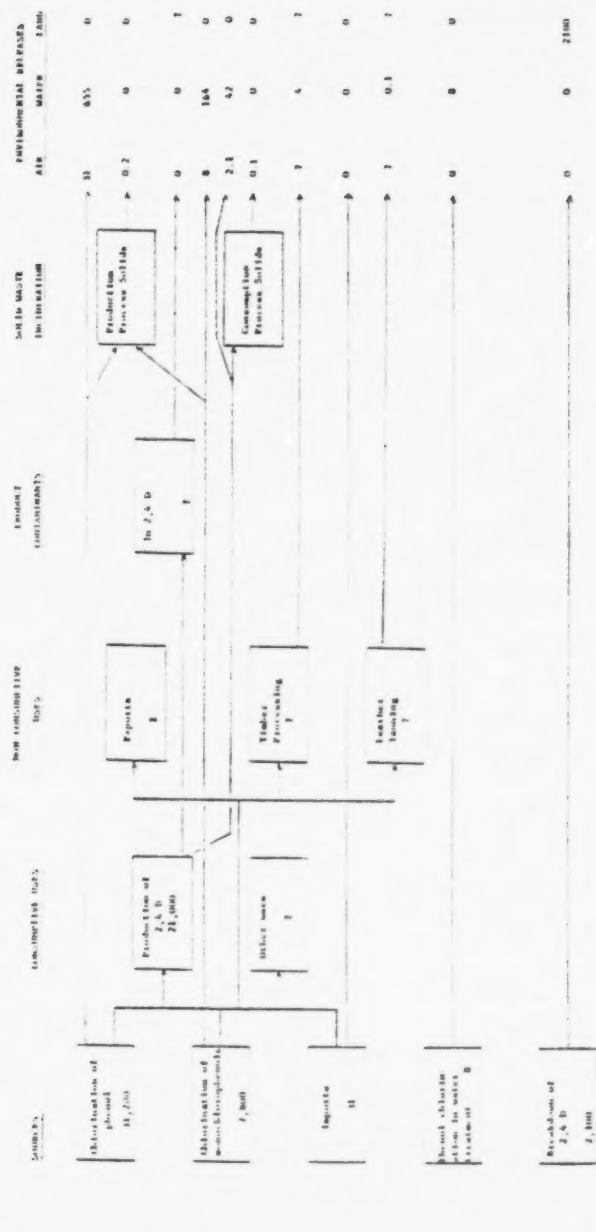
The content of 2,4-DCP in commercial preparations of 2,4-D was confidential information and could not be obtained by JRB. In order to get this information, Mrs. Willa Garner (Registration Division, OPP, 755-1397) would be contacted and given the registration number of the pesticide of interest. Mr. Jesse Mayes in Central Files (755-9315) supplied upon request the registration number of one of the hundreds of 2,4-D formulations: 464-1 is a Dow product containing 2,4-D. In addition, Ms. Alice Morgan of Dow Chemical cited a Dr. Phil Kearney at U.S.D.A. (location not known) as an authority on impurities in pesticides.

3.4.5 Degradation of 2,4-D in the Environment

2,4-D is relatively labile in the environment and can yield 2,4-DCP by either metabolic or photochemical breakdown (Kirk-Othmer, 1969). The "persistence" of 2,4-D in soils is one month (Kirk-Othmer, 1969). We have estimated the release of 2,4-DCP to soil to be 2,100 kkg in 1976, based on the following: 1) We assumed all 2,4-D produced in 1976 was used agriculturally. 2) We assumed all 2,4-D used was broken down in the soil via 2,4-DCP. 3) However, 2,4-DCP is readily degraded (Kirk-Othmer, 1969; EPA, (1975a) so that the steady-state level of 2,4-DCP was assumed to be only 10% of the 2,4-D level. The amount of 2,4-DCP present in the soil on the average at any time during the year was: $(21,000 \text{ kkg } 2,4\text{-D}) \times (0.10) = 2100 \text{ kkg}$. This value has a large uncertainty, but is included in the materials balance as an estimate of the possible contribution by this source. A materials balance on 2,4-D has probably been performed by Office of Pesticide Programs.

3.5 SUMMARY

Figure 3.3 is the materials balance diagram for 2,4-DCP. It summarizes the contributions of each process discussed to air, land, and water emissions. Emissions to water during production processes are the major source of emissions.



SOURCE: 21,000 kg
 AMOUNT: 21,000 kg
 AMOUNT PRODUCED & IMPORTED = AMOUNT CONSUMED + AMOUNT WASTED + AMOUNT STOCKED + AMOUNT EXPORTED
 21,000 kg + 0 kg = (0 kg + 0 kg + 0 kg + 0 kg) + 21,000 kg
 21,000 kg = 21,000 kg

Figure 3.3 Materials Balance for 2,4-Dichlorophenol (kg)



4.0 2,4,5-TRICHLOROPHENOL

4.1 DIRECT PRODUCTION OF 2,4,5-TRICHLOROPHENOL (2,4,5-TCP)

Figure 4.1 shows the environmental flow diagram for this chlorophenol.

4.1.1 Amounts Produced

2,4,5-Trichlorophenol was sold in commercial quantities by a number of producers in 1976, among them Dow Chemical Company, Hooker Chemical Company, Northeastern Pharmaceutical and Chemical Company and Transvaal Company (EPA, 1975a). These companies synthesized 2,4,5-TCP by the hydrolysis of 1,2,4,5-tetrachlorobenzene (EPA 1975a). Table 4.1 identifies the location of each plant.

Production quantities for trichlorophenols were company confidential information and have not been reported since 1970. Table 4.2 lists U. S. production and import quantities between 1960 and 1970. 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) and its derivatives are synthesized from trichlorophenol.

Since there were no data available after 1970, we estimated that the quantities shown on Table 4.2 for 1970 were representative of the past nine years. This estimate was based on analysis of the 2,4,5-T production in Table 4.2. The data appeared to show a pattern in which 2,4,5-T production (and therefore 2,4,5-TCP production) was returning to pre-military-use levels. The demand for 2,4,5-T probably leveled in the 1970-1976 period. Post-1976, demand and production were undoubtedly declining due to environmental regulations. In the absence of data, however, we estimated that 1976 production of 2,4,5-TCP and its derivatives was similar to the 1960 value.

The actual production of 2,4,5-TCP was extracted from Table 4.2 by making estimates about the relative amount of 2,4,5-T produced compared to its several derivatives. MRI (1972) suggested that "little" of the 2,4,5-T produced remains

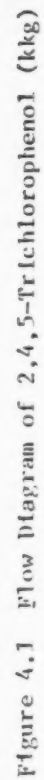


TABLE 4.1 PRODUCERS OF 2,4,5-TRICHLOROPHENOL

Company	Plant Location
Dow Chemical Company	Midland, Michigan
Hooker Chemical Company	Niagara Falls, New York
Northeastern Pharmaceutical and Chemical Company	Verona, Missouri
Transvaal Company	Jacksonville, Arkansas

TABLE 4.2 PRODUCTION AND IMPORTS OF 2,4,5-TCP AND ITS ACID,
ACID DERIVATIVES AND SALTS (EPA, 1975a, AND ENTOMA, 1975)
(kkg)

		PHENOL AND SALTS	2,4,5-T and DERIVATIVES
1960	U. S. Production U. S. Imports	4,550 N/A	6,350 N/A
1961	U. S. Production U. S. Imports	4,990 N/A	6,800 N/A
1962	U. S. Production U. S. Imports	5,440 N/A	8,620 N/A
1963	U. S. Production U. S. Imports	5,440 N/A	8,620 N/A
1964	U. S. Production U. S. Imports	6,350 N/A	10,880 N/A
1965	U. S. Production U. S. Imports	5,900 N/A	11,340 N/A
1966	U. S. Production U. S. Imports	8,160 N/A	14,990 0
1967	U. S. Production U. S. Imports	11,340 N/A	19,050 44.1
1968	U. S. Production U. S. Imports	12,700 N/A	27,220 179.4
1969	U. S. Production U. S. Imports	N/A N/A	8,160 20.6
1970	U. S. Production U. S. Imports	N/A N/A	6,350 0

TABLE 4.3 MOLECULAR WEIGHTS OF 2,4,5-TCP AND ITS DERIVATIVES

COMPOUND	MOLECULAR WEIGHT
2,4,5-Trichlorophenol	197
2,4,5-TCP Sodium Salt	219
2,4,5-T (Acid)	255
2,4,5-T Isooctylester	367

as an acid for sale. We estimated that the quantity of 2,4,5-T sold was approximately 20 percent of the total 2,4,5-T and Derivatives (6350 kkg - Table 4.2). The remaining 80 percent was assumed to be of the same molecular weight as 2,4,5-T isooctylester (see Table 4.3 for compound molecular weights used). The selection of 2,4,5-T isooctylester was made because 1100-1800 kkg of the derivative were synthesized by Thompson-Hayward Chemical Company (MRI, 1972). This represented about a third of the total 1960 sales of 2,4,5-T derivatives (80 percent of 6350 kkg). The quantity of 2,4,5-TCP contained in 2,4,5-T and Derivatives was estimated as follows:

2,4,5-T	$0.2 \times 6350 \text{ kkg} \times 197 \div 255 = 981 \text{ kkg}$
2,4,5-T derivatives	$0.8 \times 6350 \text{ kkg} \times 197 \div 367 = 2727 \text{ kkg}$
Subtotal 2,4,5-TCP	3708 kkg

This subtotal was the quantity of 2,4,5-TCP contained in the 2,4,5-T and Derivatives column of Table 4.2 in 1960.

To determine the remaining quantity of 2,4,5-TCP produced, the amount of 2,4,5-TCP contained in the Phenol and Salts column (Table 4.2) less the amount sold for use in 2,4,5-T and Derivatives were calculated.

Production quantities of 2,4,5-T for Dow and of 2,4,5-T isooctylester for Thompson-Hayward were given by MRI (1972). Using these production figures, it was estimated that approximately 45 percent of the 2,4,5-TCP contained in 2,4,5-T and Derivatives was purchased from other manufacturers. The remaining quantity of 2,4,5-TCP and Salts was:

(Phenol and Salts (Table 4.2)) - (0.45 x Subtotal of TCP for 2,4,5-T
and Derivatives)

= 2881 kkg

If the remainder was 100% 2,4,5-TCP, then the total 2,4,5-TCP was 2881 kkg + 3708 kkg = 6589 kkg. At the other extreme, if the remainder was 100% salt, then the total 2,4,5-TCP was (2881 kkg x molecular weight of phenol + molecular weight of salt) + 3708 kkg = 6300 kkg. This value will be used for further preparation of the materials balance. The error range of this value was estimated to be +5% (since the 100% 2,4,5-TCP assumption represents an upper bound) and -40% (in the case of less-than-capacity production by the two companies with available production data (MRI, 1972)).

Another method of producing 2,4,5-TCP was by the diazotization of 2,4,5-trichloroaniline. There were no sources that suggested that this method was used. Therefore, we estimated that no more than 0.2 percent of the total U. S. production was formulated in this manner.

4.2 AMOUNT IMPORTED

The amount of 2,4,5-TCP imported is not regularly reported by the USITC. ENTOMA (1975) cited the quantities through 1970. The quantity of 2,4,5-TCP imported was never greater than 0.5 percent of total production (Table 4.2). Excess U. S. production capacity due to the Viet Nam War would suggest that there were no imports of 2,4,5-TCP in 1976. In the absence of other data, we assumed that this value has been applicable for the past eight years.

4.3 EMISSIONS DUE TO PRODUCTION AND IMPORTS

4.3.1 Emissions Due to Production

Data on emissions to air, land and water during production of 2,4,5-TCP were not available in the literature. The basic approach to evaluating emissions during production of 2,4,5-TCP was to use the operation: (production in kkg) x (emission factor in kkg released/kkg produced). The ultimate sources of an emission factor are waste stream monitoring data, but in the absence of these data a best guess judgement was made based on engineering and economic principles.

An estimate of emission factors for air, water and land releases during 2,4,5-TCP production was based on the process flow diagram in Figure 4.2 (EPA 1975a). We assumed the diagram applied to all manufacturers although it was probably based on published descriptions of the Dow facility in Midland, Michigan (EPA, 1975a).

4.3.1.1 Emissions to Air

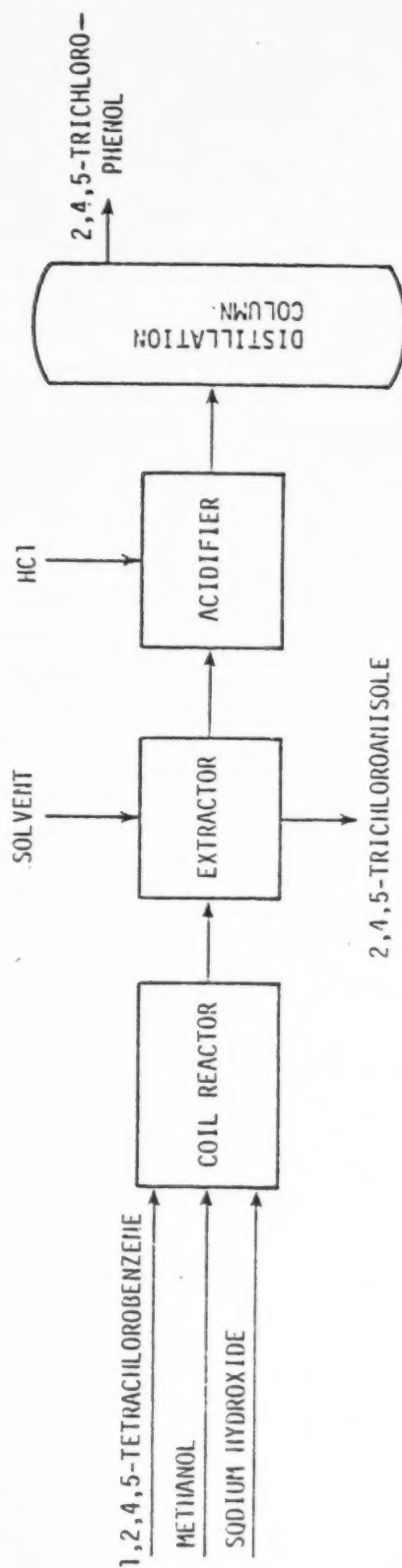
We estimated the air emission factor to be 1×10^{-3} kkg/kkg product, within an order of magnitude. This was based on air emission analysis in Section 3.3.1.1.1 (2,4-dichlorophenols). Application of this emission factor to total 2,4,5-TCP production yielded:

$$(6510 \text{ kkg}) (1 \times 10^{-3} \text{ kkg/kkg produced}) = 7 \text{ kkg 2,4,5-TCP emitted to air in 1976 due to production}$$

4.3.1.2 Emissions to Water

The water emission factor was estimated to be higher than that for air due to the large volumes of water used in the 2,4,5-TCP process, the product's sparing

FIGURE 4.2 PRODUCTION SCHEMATIC FOR 2,4,5-TRICHLOROPHENOL PRODUCTION
BY HYDROLYSIS OF 1,2,4,5-TETRACHLOROBENZENE (EPA 1975a)



solubility in water (Section 1), and the impossibility of removing all phenols in the waste streams. Data on the Dow plant were assumed to be representative of all manufacturers. Biological treatment, including trickling filter plus activated sludge, at the Dow plant was calculated to be from 90 - 100 percent efficient (Versar, 1975). Assuming that 85 percent of the 2,4,5-TCP produced was isolated, the remaining quantity entered the waste water (Section 3.3.1.1.2). The overall emission factor was:

$$(0.1 \text{ fraction not removed}) \times (0.15 \text{ fraction in waste water}) = 1.5 \times 10^{-2} \text{ kkg/}$$

kkg product or
1.5 percent
release

This factor was applied to total production to obtain water emissions:

$$(6510 \text{ kkg}) (1.5 \times 10^{-2} \text{ kkg/kkg produced}) = 98 \text{ kkg 2,4,5-TCP emitted to water}$$

due to production in 1976

This represented a near-maximum estimate if the extraction efficiency was higher than stated. The uncertainty of the water treatment emissions was proposed to be ± 50 percent.

4.3.1.3 Emissions Due to Solid Wastes

Solid residues containing phenols would be produced as heavy ends waste, sludge from wastewater treatment and ash waste from incineration.

Reactor tars were estimated to contain approximately 1×10^{-3} kkg/kkg product (Section 3.3.1.1.3).

The emission factor from sludge would be the product of efficiency of the waste treatment times the wastes lost to the water or:

$$(0.15 \text{ fraction in wastewater}) (0.9 \text{ fraction removed}) = 0.135 \text{ kkg 2,4,5-TCP} \\ \text{in sludge/kkg product}$$

However, since (by analogy to 2,4-DCP) 2,4,5-TCP is probably degradable by acclimated sludge, we estimated that the sludge contains between 1 and 10 percent of the original amount. The sludge emission factor is thus 0.00135-0.0135 kkg/kkg product.

This sludge was then incinerated and the waste gases scrubbed (MRI, 1972). Incineration efficiency varied from 95 percent (Section 3.3.1.1.3) to 99 percent (Versar, 1975) and scrubber efficiency was approximately 95 percent (Section 3.3.1.1.3). The emission factor to air for sludge treatment was:

$$(0.00135 \text{ to } 0.0135) (.01 \text{ to } .05) (.05) = 6.8 \times 10^{-7} \text{ to } 3.4 \times 10^{-5} \text{ kkg/} \\ \text{kkg product}$$

This factor was applied to total 2,4,5-TCP production and the result was added to the air emissions estimated in Section 4.2.1:

$$(6510 \text{ kkg}) (6.8 - 340 \times 10^{-7} \text{ kkg/kkg product}) = 4.4 - 220 \times 10^{-3} \text{ kkg} \\ \text{2,4,5-TCP emitted to air} \\ \text{due to solid waste incin-} \\ \text{eration in 1976}$$

4.3.2 Emissions Due to Imports

We estimated that the transport and storage of imports made a negligible contribution to total air, land and water emissions. Also, since we proposed that there are no imports at present, the losses would similarly be zero.

4.3.3 Emissions Due to Indirect Sources of Production

4.3.3.1 Emissions Due to Chlorination of Phenol-Containing Water

An upper limit on the quantity of 2,4,5-TCP produced in this process was calculated using the following: 1) The National Organics Monitoring Survey (NOMS) (EPA, 1977) reported that 2,4,5-TCP was detected although not quantifiable in U. S. drinking water samples. 2) The annual usage of water in the U. S. is 4.169×10^{13} liters per year (Metcalf and Eddy, 1972, and Section 3.3.3.1). 3) In order to give a maximum estimate, we assumed that the minimum level quantified by NOMS (0.01 mg/liter) was contained in the entire U. S. water supply.

The maximum quantity present was estimated to be:

$$(4.169 \times 10^{13} \text{ liters/year}) (0.01 \text{ mg/liter}) (10^{-9} \text{ kkg/mg}) = 400 \text{ kkg per year}$$

4.4 EMISSIONS DUE TO CONSUMPTION AND USE

4.4.1 Amounts of 2,4,5-Trichlorophenoxyacetic Acid and Derivatives and Trichlorophenol Sodium Salt Produced

Data on production of 2,4,5-T and derivatives and 2,4,5-TCP sodium salt are shown in Table 4.2. Figure 4.1 identifies those quantities of 2,4,5-TCP used to synthesize each compound. These quantities were previously calculated in Section 4.1. Data were not available on the amount of 2,4,5-TCP and all derivatives made by individual companies.

4.4.2 Emissions to the Air

2,4,5-TCP can be vented to the air during the synthesis of its derivatives. We estimated that nearly 0.5 kkg annually was emitted during these processes. In the absence of direct data on emissions or emission factors to the air, we estimated an emission factor of 1×10^{-4} kkg/kg 2,4,5-TCP used during synthesis of derivatives. The basis for this estimate was as follows: 1) We assumed that the production processes for 2,4,5-T, its derivatives and 2,4,5-TCP sodium salt are generally similar to those of 2,4,5-TCP synthesis. 2) We noted that Dow Chemical, a major 2,4,5-TCP producer, synthesized 2,4,5-T and other derivatives at its Midland, MI, plant; therefore, the emission control characteristics considered for 2,4,5-TCP synthesis also applied to 2,4,5-T synthesis. 3) In Section 4.2, we estimated the emission factor for release of 2,4,5-TCP to air during 2,4,5-TCP production to be 1×10^{-3} kkg/kg product. 4) The release factor during consumption should be about one order of magnitude smaller, because (a) most of the 2,4,5-TCP was consumed in the first step of each process, and (b) unreacted 2,4,5-TCP would be captured and recycled. We therefore estimated that an emission factor of 1×10^{-4} kkg/kg 2,4,5-TCP used during synthesis of its derivatives was appropriate within an order of magnitude. Application of this emission factor to the synthesis of 2,4,5-TCP derivatives yielded:

$$(5010 \text{ kkg}) (1 \times 10^{-4} \text{ kkg/kg}) = 0.5 \text{ kkg to the air annually}$$

4.4.3 Emissions to Water

Again, no direct information was available on releases to water during 2,4,5-TCP derivative synthesis. However, published emission factors for waste

streams from anonymous plants producing 2,4,5-T have permitted an extrapolation of 2,4,5-TCP releases to water. The amount released to water during synthesis of 2,4,5-TCP derivatives was estimated to be 11 kkg per year. This emission was based on an emission factor of 2.18×10^{-3} kkg/kg product, which was estimated as follows: 1) EPA (1976a) published monitoring data for an anonymous plant producing 2,4,5-T and presented the results as emission factors for phenols (assumed: total phenols) in the waste streams. The values were: 1.61 kg phenols/kg 2,4,5-T product (a daily average) and 2.75 kg/kg (a daily composite). 2) We had no reason a priori to discard either of the values. 3) Therefore, we used the average of these values. 4) In using this average, we were assuming that all "phenol" is 2,4,5-TCP. The emission factor was therefore a maximum value. The emission factor for release of 2,4,5-TCP to water during derivative synthesis was 2.18×10^{-3} kkg/kg product. Emissions were obtained by the operation:

$$(5010 \text{ kkg produced}) \times (2.18 \times 10^{-3} \text{ kkg/kg}) = 10.9 \text{ kkg 2,4,5-TCP released to water in 1976 due to consumptive uses}$$

The uncertainty of the emission factor was estimated to be + 5 percent, - 90 percent (since it was a maximum). The production value for 2,4,5-TCP was a maximum value also. Therefore, the amount of emissions (10.9 kkg/year) was a maximum, and had an estimated uncertainty of + 5 percent, - 95 percent.

4.4.4 Emissions Due to Disposal of Solid Residues

Direct data were not available on emissions due to disposal of solid residues from 2,4,5-TCP derivative production. These residues would be formed as reactor

tars, and as biological waste water treatment sludge. We estimated a total release to air due to incineration of solids containing 2,4,5-TCP to be negligible (<0.5 kkg). This estimate was based on the following: 1) We assumed the efficiencies estimated in Section 4.3.1.3 for disposal of solid residues during 2,4,5-TCP production were valid for 2,4,5-TCP derivatives production in the same or a similar plant. 2) The only modification was that there would be less 2,4,5-TCP in the sludge because 2,4,5-TCP was consumed in the first step of the process. 3) The overall emission factor for reactor tar would be the same as for 2,4,5-TCP synthesis: 3.4×10^{-5} kkg/kg product. 4) The emission factor for biological treatment sludge would be 5-fold lower:

$$(3.4 \times 10^{-5} \text{ kkg/kg product}) \times (0.2) = 6.8 \times 10^{-6} \text{ kkg/kg product}$$

Applying these emission factors to 2,4,5-TCP derivative synthesis yielded the emission amounts:

$$\begin{aligned} (3.4 \times 10^{-5} \text{ kkg/kg}) \times (5010 \text{ kkg}) &= 0.17 \text{ kkg from tars} \\ (6.8 \times 10^{-6} \text{ kkg/kg}) \times (5010 \text{ kkg}) &= 0.034 \text{ kkg from sludge} \end{aligned}$$

The sum was 0.2 kkg of 2,4,5-TCP released to air due to disposal of solid residues. This is entered on Figures 4.1 and 4.3 as ~0 kkg.

4.4.5 Degradation of 2,4,5-TCP in Derivatives

2,4,5-TCP derivatives are relatively labile in the environment and can yield 2,4,5-TCP by either metabolic or photochemical breakdown (Kirk-Othmer, 1969). For example, the "persistence" of 2,4,5-T in soils is five months

(Kirk-Othmer, 1969). We have estimated the release of 2,4,5-TCP to soil to be 100 kkg in 1976, based on the following: 1) We assumed all 2,4,5-T and other derivatives produced in 1976 were used agriculturally. 2) We assumed all 2,4,5-TCP derivatives used were broken down in the soil via 2,4,5-TCP. 3) However, 2,4,5-TCP is readily degraded (Kirk-Othmer, 1969; EPA, 1975a) so that the steady-state level of 2,4,5-TCP was assumed to be only 2 percent of the level of 2,4,5-TCP derivatives. The amount of 2,4,5-TCP present in the soil on the average at any time during the year was:

$$(5010 \text{ kkg } 2,4,5\text{-TCP derivatives}) (0.02) = 100 \text{ kkg}$$

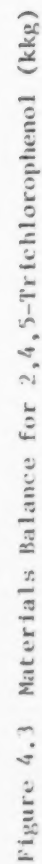
This value had a large uncertainty, but was included as an estimate of the possible contribution by this source. A materials balance on 2,4,5-T is probably on file at the Office of Pesticide Programs. This materials balance would improve the estimate of the quantity of 2,4,5-TCP in the environment due to degradation.

4.4.6 Direct Use of 2,4,5-TCP

2,4,5-TCP was used directly as a fungicide, preservative and antimildew treatment. Information on the distribution and method of application was not readily available. As an upper limit, we estimated 1300 kkg (the total quantity of 2,4,5-TCP not converted to other products) would be released. This would take place either by direct application (fungicide) or by the disposal of products treated with 2,4,5-TCP (preservative or antimildew). Without further data, it was impossible to quantify the specific releases to air, land or water for the phenol.

4.5 SUMMARY

Figure 4.3 is the materials balance diagram for 2,4,5-TCP. It summarizes the contributions of each process discussed to air, land, and water emissions.



5.0 TETRACHLOROPHENOL

Tetrachlorophenol was not produced as a separate chemical in 1976. Rather, it was a by-product, mostly as the 2,3,4,6-isomer in commercial pentachlorophenol (PCP) (Federal Register, 1978). Its concentration in PCP has been reported to range from 4 to 10 percent by weight. Its physical properties are not drastically different from those of pentachlorophenol (see Chapter 1). For the above reasons, the materials balance for tetrachlorophenol was estimated using the same assumptions and information which are discussed in Chapter 6, the chapter on pentachlorophenol.

Figure 5.1 presents the summary of the materials balance for tetrachlorophenol. The emission factors to air, water and land were assumed to be the same as those used in the PCP chapter for each process and end use.

The annual production of tetrachlorophenol was estimated at 8 percent of PCP production, or 1800 kkg in 1976. The major indirect source was the release to land from stockpiles, i.e., leaching from preserved wood utility poles. Those releases were estimated at 770 kkg in 1976 based on the PCP discussion in Chapter 6.

Uses of PCP contaminated with tetrachlorophenol as a fungicide, herbicide and in home and garden applications also accounted for significant releases of tetrachlorophenol. Those include 6.3 kkg to air, 13 kkg to water, and 41 kkg to land. Next in order of importance were the releases from the production of PCP, which amounted to 1.8 kkg to air and 53 kkg to water in 1976. JRB estimated that total releases of tetrachlorophenol to air were between 8.7 and 98 kkg, those to water were 67 to 160 kkg, and those to land from 44 to 130 kkg in 1976.

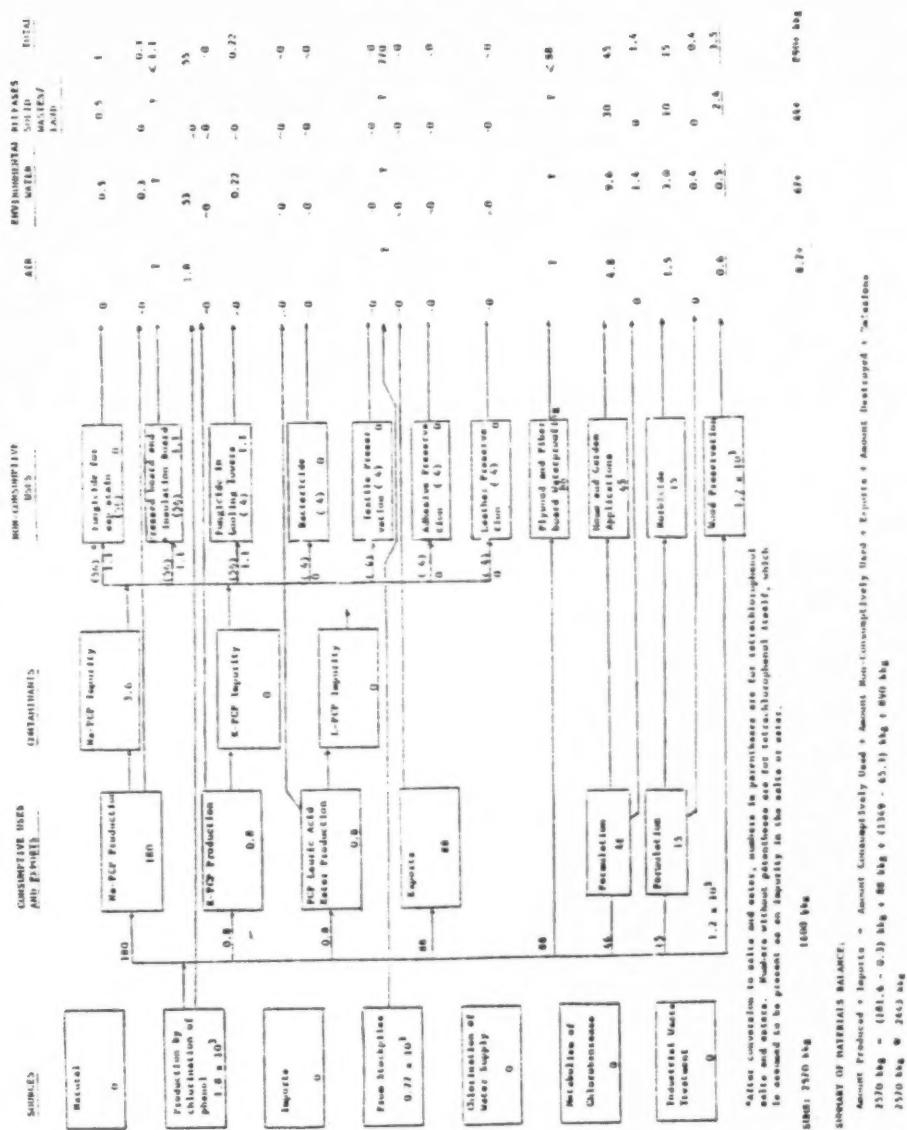


Figure 5.1 Materials Balance for Tetrachlorophenol (t.kg)

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6.0 PENTACHLOROPHENOL (PCP)

This chapter discusses the materials balance, production statistics, consumption and uses information for pentachlorophenol (which include the production of pentachlorophenol salts, and the lauric acid ester of PCP), and presents estimates of releases to land, air and water.

6.1 ENVIRONMENTAL FLOW DIAGRAM FOR PCP

Figure 5.1 shows the flow diagram for PCP based on the 1978 estimate of 22,000 kkg of PCP produced in the U. S. (Versar, 1979) and the 1978 export figure of 1100 kkg (Bureau of Census, 1978). No information on imports was reported in the available literature.

Natural sources contributed insignificant emissions. The major indirect sources of emissions included releases to land from stockpiles, which consisted mostly of leaching from preserved wood poles. Those releases were estimated to be 9,600 kkg per year. Uses of PCP as a fungicide, herbicide, and home and garden applications also accounted for significant annual emissions. Those included 80 kkg to air, 506 kkg to land, and 154 kkg to water. Next in order of importance were the emissions from the direct production of PCP, which amounted to 12 kkg per year to air and 660 kkg per year to water.

JRB estimated that the environmental releases of PCP from direct sources to air totaled 120-720 kkg, those to water were 800-1400 kkg, and those to land were 500-1100 kkg. The basis for those estimates is presented in the sections below.

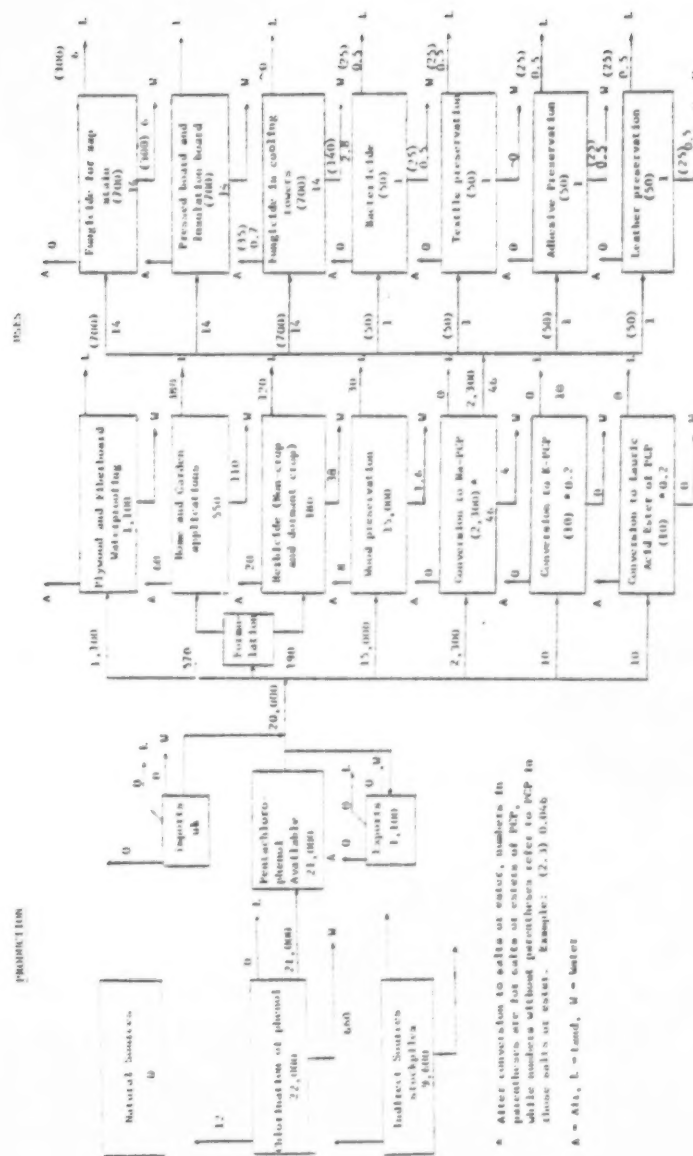


Figure 6.1 Flow Diagram for Pentachlorophenol (kg)

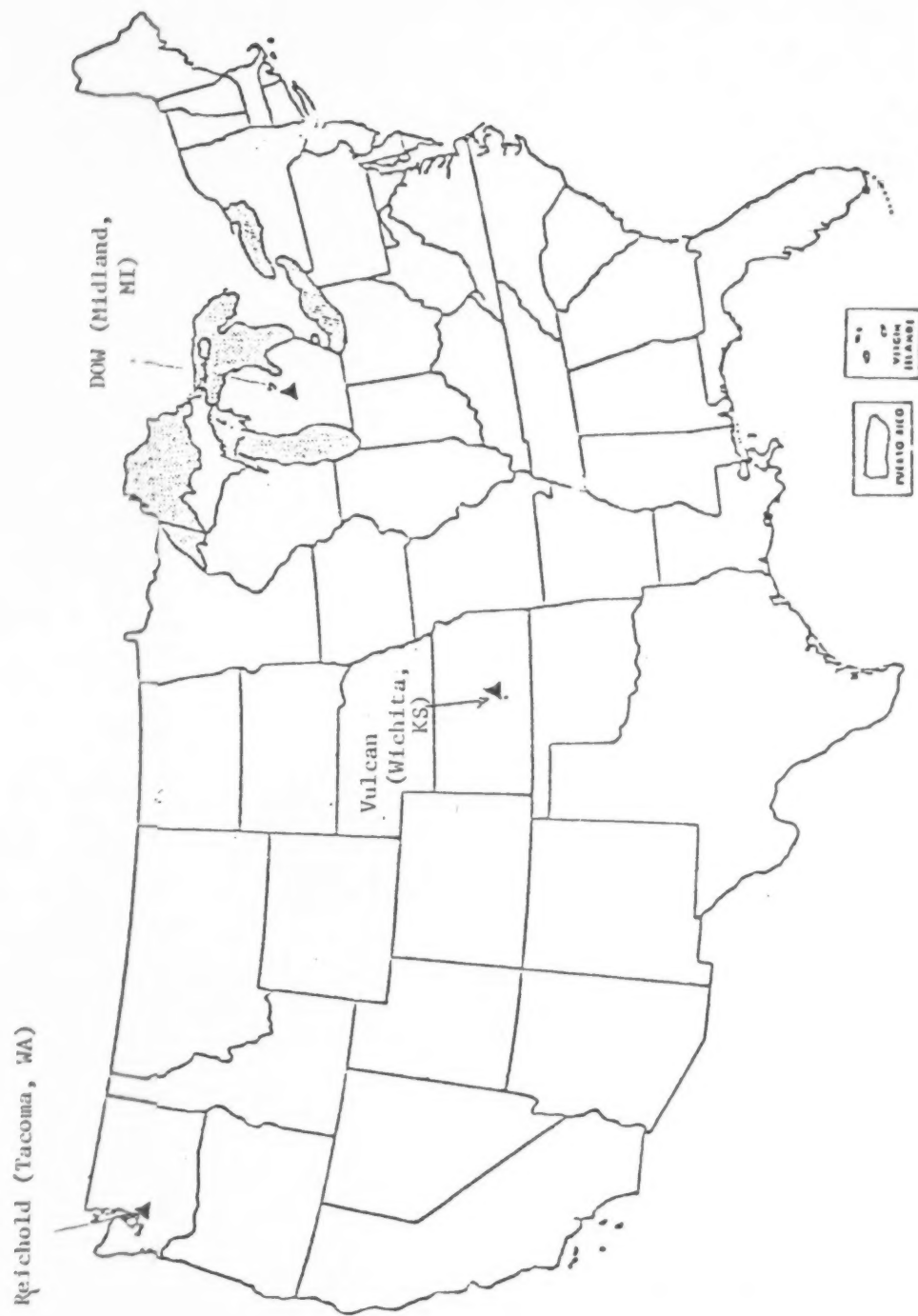


Figure 6.2 Pentachloropheno1 Producers

6.2 PRODUCTION

PCP has been marketed since 1930 in the U. S. Table 6.1 shows the producers of PCP, their locations and capacities in 1978. Monsanto discontinued their PCP production in 1978, and thus is not shown. Monsanto's capacity prior to 1978 was 12,000 kkg per year. Figure 6.2 shows the geographic distribution of the PCP producers (Tracor-Jitco, 1976b). The estimated supply and demand for PCP are shown in Table 6.2 (Versar, 1979). During the 1960s, production of PCP grew at a rate of 2 percent per year -- from about 17,700 kkg to about 21,300 kkg. In the 1970s, the production of PCP has remained relatively unchanged, except in 1974 and 1975.

The data on plant capacity were compatible with a 1977 memorandum prepared by the American Wood Preservers Institute, and hence appear valid. The production statistics through 1977 were compatible with those published by the U. S. International Trade Commission. The demand estimates appeared reasonable because they are usually equal to, or slightly greater than the production statistics for any single year, and also because the production in the following year was shown to have increased in order to meet the demand level for the previous year.

Table 6.1 Pentachlorophenol Producers

<u>Producer</u>	<u>Location</u>	Capacity in 1978
		<u>kkg</u>
Dow	Midland, MI	11,000
Reichold	Tacoma, WA	9,100
Vulcan	Wichita, KS	7,300

Table 6.2

ESTIMATED SUPPLY AND DEMAND FOR PENTACHLOROPHENOL
(IN KKG.)

	<u>1960</u>	<u>1965</u>	<u>1970</u>	<u>1973</u>	<u>1974</u>	<u>1975</u>	<u>1976</u>	<u>1977</u>	<u>1978</u>	<u>1979</u>	<u>1981</u>
Capacity		25,400		35,400	31,300	33,100	33,100	33,100	27,700	27,700	
Production	17,800	19,800	21,400	21,100	23,700	17,900	19,900	20,400	21,300		
Demand	17,800	19,800	21,400	21,100	23,700	17,900	20,000	21,300	21,300	21,300	23,100

SOURCE: Versar, 1979

Approximately 60 formulators were registered with EPA for products containing PCP. Their names and addresses were listed in the Federal Register (1978). As for indirect sources, pentachlorobenzene has been shown to be metabolized in rats to give PCP (EPA, 1975a). No quantitative estimate of this process was found in the available literature, but it was assumed to be insignificant compared to industrial production. Chlorination of water containing phenol does not result in PCP (EPA, 1975b).

6.3 CONSUMPTION AND USES

The flow pattern for PCP use is included in Figure 6.1 which also summarizes the environmental releases for PCP. The end use pattern was based on information gathered from EPA (1975a), Tracor-Jitco (1977b), and Versar (1979). No major discrepancy among those references was found.

As shown, PCP was used mostly in the preservation of wood and the production of sodium pentachlorophenate. Pentachlorophenol used in wood preserving accounted for 78 percent of total PCP production. Twelve percent of the PCP produced was used for sodium pentachlorophenate (Na-PCP) production. The USITC listed Dow as the only producer of Na-PCP in 1976. Sodium pentachlorophenate was used mainly as a fungicide and bactericide. Since no information was available as to the uses for potassium pentachlorophenate, we have assumed that it was used similarly to the sodium salt because of chemical similarity between the two. No uses were reported in the available literature for the lauric acid ester, although it was a registered pesticide product. We have assumed that production of these compounds was limited, amounting to 10 kkg annually for each compound. This was compatible with the information from Federal Register (1978), which showed that 0.6 percent of registered PCP products contain

potassium pentachlorophenate, and 0.8 percent contain PCP lauric acid ester. The remaining 10 percent of the PCP was used in miscellaneous applications, including several minor ones and three major ones which were: (a) to waterproof fiberboard and plywood, (b) in home and garden applications, and (c) as an herbicide. The following sections discuss those end uses for which information was available.

6.3.1 Wood Preservation

Figure 6.3 shows the location of wood preservation plants (Environmental Science and Engineering, 1978). Table 6.3 lists the quantity of wood products treated with PCP in 1975 (AWPI, 1977). From the table, it is seen that most of PCP was used for the treatment of poles and lumber. The AWPI report showed that the total amount of wood treated with PCP was 61 MM cubic feet in 1975. JRB estimated that 15,000 kkg of PCP were used by the industry (see Figure 6.1).

6.3.2 Pressed Board and Insulation Board Manufacture

Figures 6.4 and 6.5 are maps showing the geographic locations of the plants producing pressed board and insulation board (Environmental Science and Engineering, 1978). Based on Versar's 1979 draft on pentachlorophenol, close to one third of the sodium pentachlorophenates was consumed by this industry, i.e., 700 kkg of PCP went to the sodium salt which was used by the pressed board and insulation board industry.

6.3.3 Other PCP Uses

After accounting for the three principal uses of the PCP salts, which were reported (Versar, 1979) as: (a) treatment of sap stain which occurred on unseasoned logs, (b) pressed board and insulation board manufacture, and (c)

FIGURE 6.3

GEOGRAPHICAL DISTRIBUTION OF WOOD PRESERVING PLANTS IN THE UNITED STATES

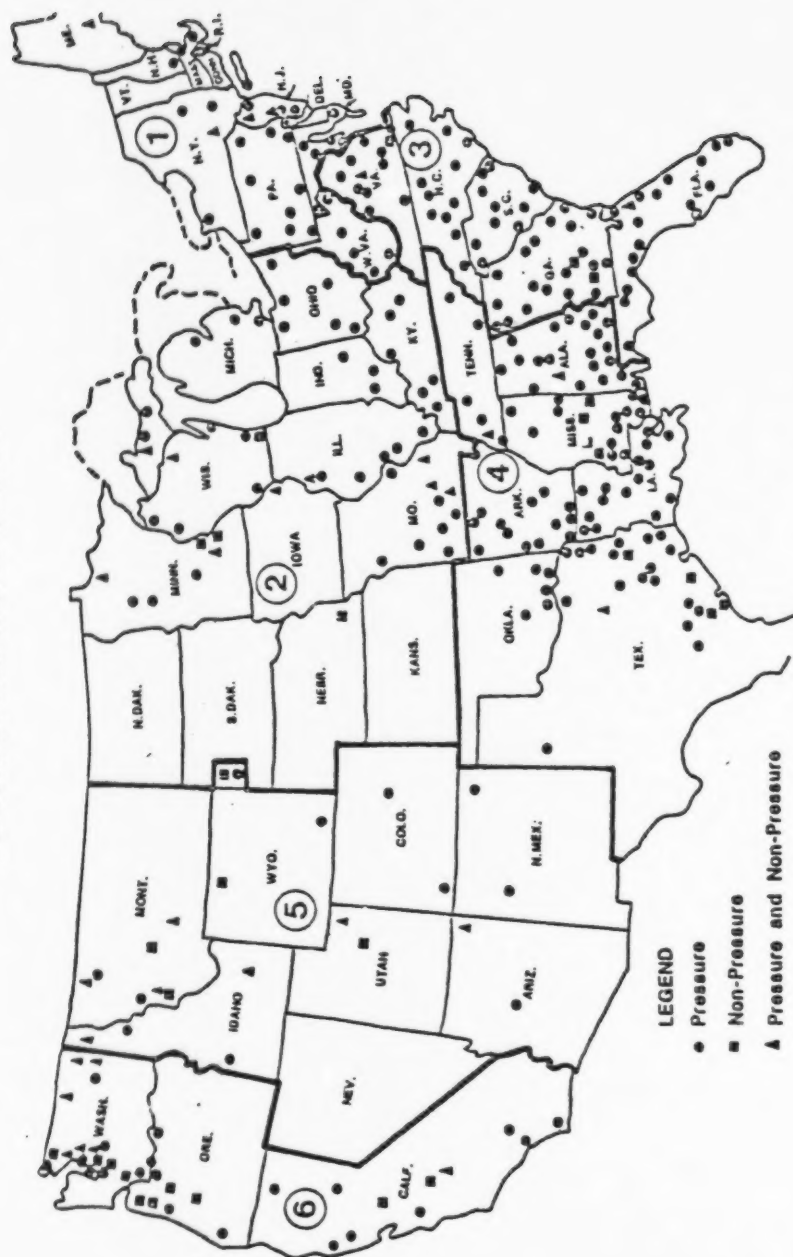


Table 6.3 Quantities of Wood Products
Treated with Pentachlorophenol,
1975

	<u>QUANTITY TREATED</u>		<u>PROPORTION TREATED</u>
	Total	With Penta	WITH PENTA
	<u>Million cu ft</u>		<u>%</u>
Railway ties	101.1	0.4	0.4
Poles	49.1	32.2	65.0
Piling	9.4	0.4	4.0
Lumber*	62.9	17.1	27.0
Fence posts	15.3	10.0	65.0
Other	<u>6.3</u>	<u>0.8</u>	13.0
	244.1	60.9	24.9

* Includes timbers and crossarms

[NOTE: Components may not add to totals due to rounding.]

SOURCE: AWPI, 1977

FIGURE 6.4

GEOGRAPHICAL DISTRIBUTION OF HARDBOARD MANUFACTURING FACILITIES IN THE UNITED STATES

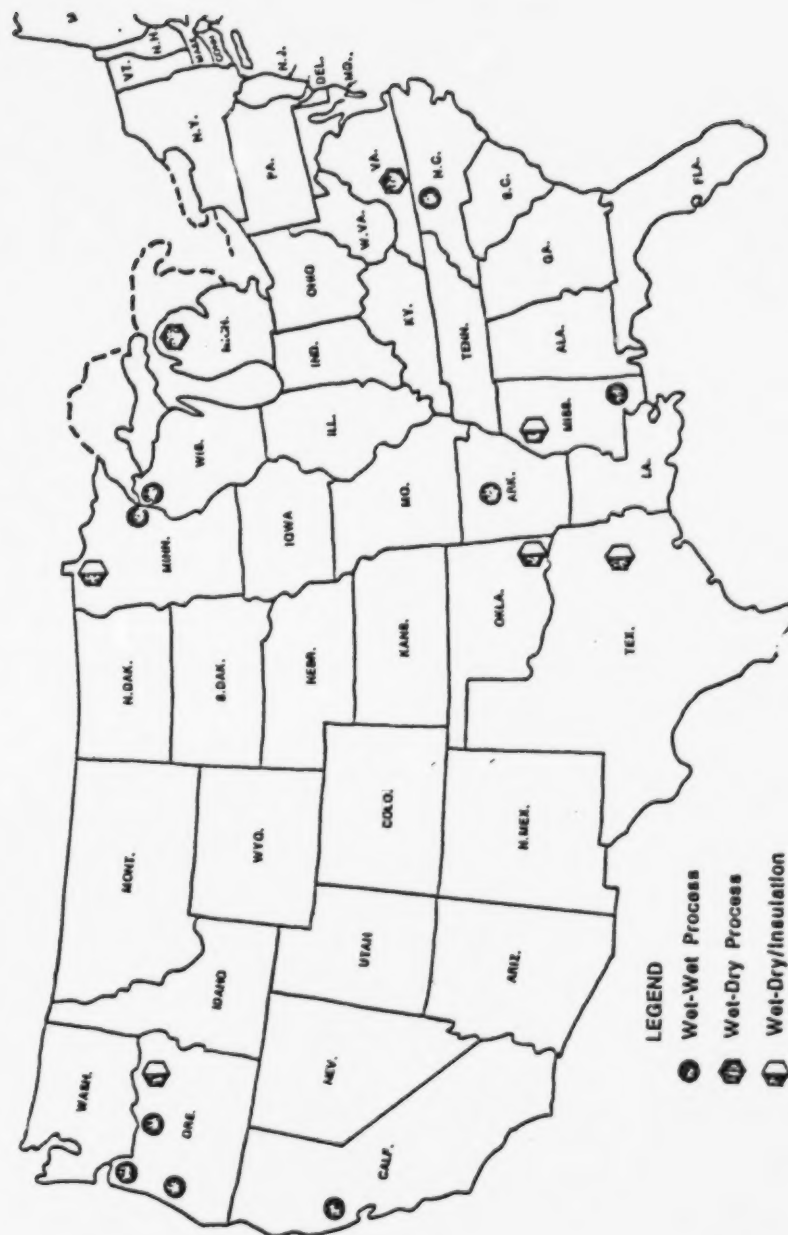
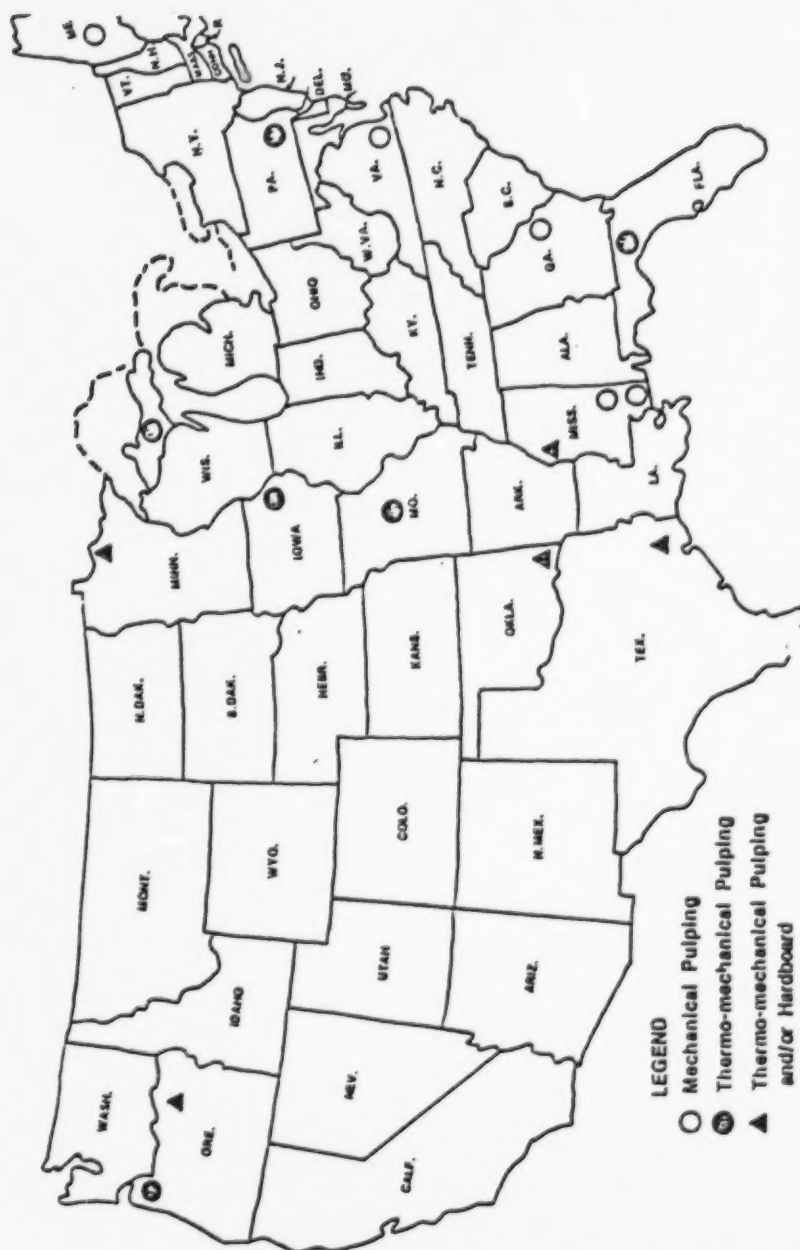


FIGURE 6.5

GEOGRAPHICAL DISTRIBUTION OF INSULATION BOARD MANUFACTURING FACILITIES IN THE UNITED STATES



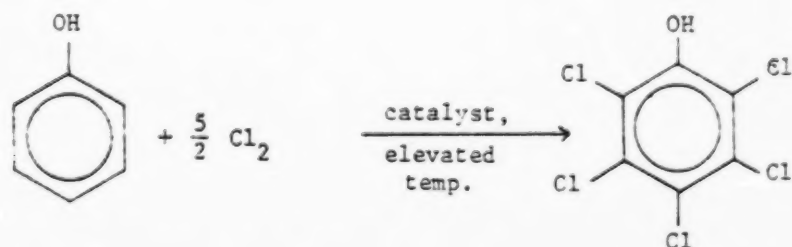
prevention of slime and mold in cooling towers, it was estimated by JRB that only 200 kkg of PCP were consumed as sodium salt in minor uses as bactericides, and for the preservation of textiles, adhesive, and leather. As no information was reported in the available literature regarding the amount going to each end use, and since those account for a minor portion of the PCP salt, JRB estimated that each of those minor uses accounted for 50 kkg of PCP per year.

For the PCP that was not converted to salts, based on the percentage going to each end use as reported by Versar (1979), JRB estimated that 1100 kkg were used in plywood and fiberboard waterproofing, 570 kkg were used in home and garden applications (control of termites, preservative in paints for porch and lawn furniture, trailers and boats, and bird repellent which was applied to trees), and 190 kkg were used as an herbicide (mostly in non-crop areas and dormant crop areas).

6.4 EMISSIONS TO THE ENVIRONMENT

6.4.1 Production of PCP

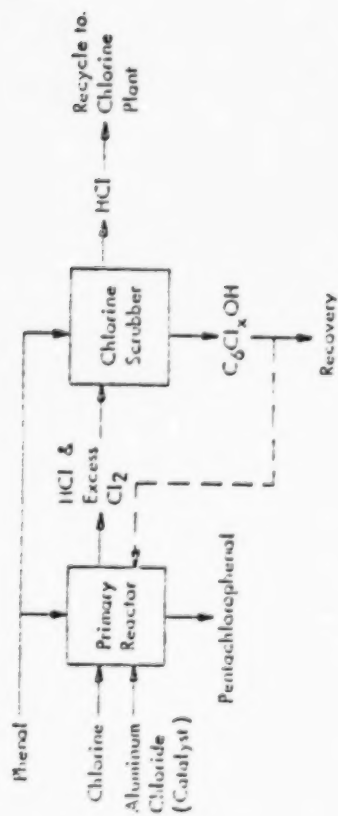
This section discusses the production process and presents estimates of environmental releases. Pentachlorophenol is produced by the chlorination of phenol. The reaction chemistry is shown below:



In PCP production, the chlorination reaction is performed at atmospheric pressure. The temperature of the phenol in the primary reactor at the beginning of the reaction is in the range of 65-130° C. Then a metallic chloride catalyst, such as ferric chloride or aluminum chloride, is added and the temperature is progressively increased to maintain a temperature of about 10° C over the product's melting point. The product is a mixture of tri-, tetra- and pentachlorophenols, with the proportion of PCP increasing with time at the expense of the other two chlorophenols. The reaction is completed in 5 to 15 hours. The off-gas for the chlorination reactor (mainly HCl) is sent to a scrubber reactor containing phenol. It is held at a temperature such that the chlorine is essentially depleted by reacting with phenol and forming a mixture of lower chlorinated phenols. This material is normally recycled to the PCP reactor. The residual gas is pure HCl. The production process is illustrated in Figure 6.6.

6.4.1.1 Air Emissions

PCP has a relatively low vapor pressure. At the highest temperature that can be expected in the reactor (200° C), its vapor pressure was calculated to be only 26.3 mm Hg based on a correlation shown in the CRC Handbook of Chemistry and Physics. Thus, the quantity of PCP in vapor form which was emitted to air would be small. For PCP particulates, an upper bound was given in EPA (1978), at 5.5×10^{-4} kkg pollutant/kkg product. This was considered an upper bound because that emission factor also included particulates from fuel combustion. No rationale was given in that report as to how the number was derived, but the author cited two references which he used. Thus, particulate emissions were estimated as:



SOURCE: AMP1, 1977

Figure 6.6 Production Process for Pentachlorophenol

$$(22,000 \text{ kkg PCP}) (5.5 \times 10^{-4} \frac{\text{kkg}}{\text{kkg}}) = 12 \text{ kkg of PCP particulate per year}$$

Since this was an upper bound estimate, the uncertainty was + 50 percent,
- 90 percent.

Because the biodegradation rate for PCP was slower than that of dichlorophenol (EPA, 1975a), an emission factor into the sludge was estimated at 2×10^{-3} kkg/kkg of PCP product, as compared to an estimated factor of 1.3×10^{-3} kkg/kkg for 2,4-DCP (see Chapter 3). Assuming a 95 percent incineration efficiency for this sludge, followed by scrubbing at 95 percent efficiency, the amount of PCP released to the air from sludge treatment was estimated as follows:

$$(22,000 \text{ kkg}) (2 \times 10^{-3} \text{ kkg/kkg}) (0.05 \text{ fraction not incinerated}) \times \\ (0.05 \text{ fraction not scrubbed}) = 0.11 \text{ kkg of PCP released to air due to production}$$

The amount returned to the plant in the scrubber water was assumed to be sent to the wastewater treatment unit.

6.4.1.2 Water Emissions

Based on a plant study with respect to 2,4-D production at Dow, dikes have been used around production/storage areas to prevent spills. Dow also has a holding pond which is automatically switched in during emergencies (MRI, 1972). Therefore, in the absence of better information, it was assumed that risk of releases from spillage was negligible for PCP plants. PCP has been shown to

degrade in activated soil more slowly than 2,4-DCP (EPA, 1975a), therefore the water emission was estimated to be higher than that of 2,4-DCP, (estimated in Chapter 3) or approximately 0.03 kkg emitted per kkg product, with an uncertainty of +50%, -90%, or:

$$(22,000 \text{ kkg PCP}) \left(\frac{0.03 \text{ kkg PCP release}}{\text{kkg PCP produced}} \right) = 660 \text{ kkg PCP to water in 1978}$$

6.4.1.3 Solid Waste Disposal

In a Midwest Research Institute survey, Dow reported that they had on-site quality control laboratory facilities, and frequently monitored the raw materials and reaction intermediates as well as the final product (MRI, 1972). MRI hypothesized that production runs that were so far "off-specification" that they needed to be discarded would be extremely rare. Therefore, JRB assumed that this source of release was 0.1 percent of production rate. Reactor tars would contribute another 0.1 percent at the maximum. This estimate by JRB was based on economics because a relatively high PCP content in tars would suggest that some sort of tar reclaiming would be carried out and thus would result in a low PCP content in tars. PCP in solid waste was estimated as:

$$(22,000 \text{ kkg PCP}) (0.002 \text{ kkg/kkg}) = 44 \text{ kkg PCP emitted in solid wastes due to production}$$

Assuming 90 percent was incinerated, the amount going to landfill was:

$$(44 \text{ kkg}) (0.1) = 4.4 \text{ kkg PCP-containing residues to landfill}$$

The PCP emitted to air from the incineration process was:

(0.05 fraction surviving incineration) (0.05 fraction not scrubbed) x
(39.6 kkg) = 0.10 kkg PCP emitted to air due to disposal of solid wastes

This was negligible compared to the particulate emission from processing as discussed in the section on air emissions.

6.4.2 Formulations of PCP Product

PCP in the solid form produced by manufacturers was formulated into solutions or briquettes. Some of the formulations were reported in the Federal Register (1978). Since pesticides and herbicides also exist as dusts, PCP could also conceivably be formulated into dust form. Lacking adequate information in this Level I study, JRB assumed that the environmental releases at formulating plants were similar to those from production plants. JRB assumed that major users purchase the PCP in bulk as a solid, whereas the PCP used in home and garden applications, and as an herbicide is formulated. The emissions thus calculated are shown in Figure 6.1.

6.4.3 Distribution and Storage of PCP and PCP Derivatives

The movement of PCP from the three manufacturers to the end-users involved transportation, warehousing, redistribution and storage or shelving at the point of purchase. Losses during distribution have been estimated by MRI (1972) to be between 0.01 and 0.1 percent for pesticides. PCP is shipped by producers as a prilled solid in bags, a pelleted solid in bags and in bulk, and in one-half and one-ton blocks with a metal hook cast in the center. Bags and solid blocks are shipped in trucks and freight cars, bulk shipments are by hopper trucks

and railroad cars (AWPI, 1977). JRB assumed an average emission factor of 0.05 percent:

$$(20,000 \text{ kkg PCP}) (0.0005 \text{ kkg/kg}) = 10 \text{ kkg PCP emitted due to distribution in 1978}$$

JRB also estimated that 95 percent of the shipments were by truck and rail, and 5 percent by water transport. Therefore, 9.5 kkg were released to land and 0.5 kkg was released to water.

6.4.4 Environmental Releases from Uses

The following sections discuss the releases from various uses of PCP.

6.4.4.1 Production of PCP Salts and Lauric Acid Ester

No information was available as to the production and formulation of PCP derivatives. Assuming 98 percent yield in the production of PCP derivatives, the PCP present as a contaminant would be an order of magnitude less than in the production of PCP itself. Therefore, in this case, the emission factors for PCP would be an order of magnitude smaller than those estimated in Section 6.4.1.

Thus, air emissions of PCP were estimated at 5×10^{-5} kkg per kkg of PCP derivative produced, resulting in negligible emissions for the production of the relatively small amounts of Na-PCP, K-PCP and lauric acid ester. Similarly, water emissions were estimated at 1.5×10^{-3} kkg per kkg PCP derivative. Production of Na-PCP resulted in the following estimated release to water:

$$(2300 \text{ kkg PCP}) \frac{(1.15 \text{ kkg Na-PCP})}{\text{kkg PCP}} \frac{(1.5 \times 10^{-3} \text{ kkg PCP lost})}{\text{kkg Na-PCP produced}} = 3.97 \text{ kkg PCP emitted to water due to derivative synthesis}$$

The release from the K-PCP and lauric acid ester production was negligible because the quantity of Na-PCP produced was much larger than the other two. Assuming incineration of solid waste, land release would be negligible.

6.4.4.2 Herbicide and Home and Garden Applications

When PCP was used as a herbicide, essentially all of that PCP was released to the environment. Versar (1979) assumed that 10 percent goes to air, 20 percent to water, and 70 percent to land. The authors did not explain how they came up with the estimate. Nevertheless, it appeared a reasonable first cut attempt at quantifying the releases to the three media. Thus, for the 180 kkg of PCP that were used as an herbicide, 20 kkg went to air, 38 kkg went to water and 120 kkg were released to land.

For home and garden uses, Versar assumed the same distribution to air, land and water as above. This resulted in an estimate of 60 kkg to air, 390 kkg to land, and 120 kkg to water on an annual basis. The validity of the estimate could not be checked in this Level I study because there was not enough information in the available literature. The assumption of total release may have been too conservative, because PCP used with paint on porch and lawn furniture, for example, would appear to remain attached to the surface of the wood for some length of time.

6.4.4.3 Wood Preservation

Versar (1979) estimated that 1 kkg of PCP was released to water and 4 kkg discharged to publicly-owned treatment works. Environmental Sciences and

Engineering reported in a 1978 study that the treated effluents from wood preserving plants contained an average of 0.082 lb PCP per 1000 cubic feet, and untreated discharges contain 0.383 lb PCP per 1000 cubic feet. From the data reported in the ES & E study, JRB calculated that an average of 1.14 gallons of waste water per day was generated per cubic foot of preserved wood.

The total annual PCP discharge from wood preserving plants was:

a) lower bound (assuming all plants discharge treated effluents)

$$\left(\frac{0.082 \text{ lb PCP}}{1000 \text{ ft}^3 \text{ water}} \right) \left(\frac{1.14 \text{ gallon water}}{1 \text{ ft}^3 \text{ wood}} \right) \left(\frac{0.13368 \text{ ft}^3 \text{ water}}{\text{gallon water}} \right) \left(\frac{61 \times 10^6 \text{ ft}^3 \text{ wood}}{\text{year}} \right) \times$$

$$\left(\frac{1 \text{ kkg}}{2200 \text{ lb PCP}} \right) = 0.35 \text{ kkg/year}$$

b) upper bound (assuming all plants discharge untreated effluents)

$$\left(\frac{0.383 \text{ lb PCP}}{1000 \text{ ft}^3 \text{ water}} \right) \left(\frac{1.14 \text{ gallon water}}{1 \text{ ft}^3 \text{ wood}} \right) \left(\frac{0.13368 \text{ ft}^3 \text{ water}}{\text{gallon water}} \right) \left(\frac{61 \times 10^6 \text{ ft}^3 \text{ wood}}{\text{year}} \right)$$

$$\left(\frac{1 \text{ kkg}}{2200 \text{ lb PCP}} \right) = 1.6 \text{ kkg/year}$$

JRB's estimates using the results of the ES & E report are compatible with the estimates made by Versar. No information was given for air and land releases, and hence JRB assumed that the emission factors were similar to those at producing plants.

Release to air:

$$\frac{15,000 \text{ kkg}}{\text{year}} (5.5 \times 10^{-4} \text{ kkg/kg}) = \frac{8.3 \text{ kkg PCP particulate}}{\text{year}}$$

Solid Wastes:

$$\frac{15,000 \text{ kkg}}{\text{year}} (0.002) = \frac{30 \text{ kkg PCP}}{\text{year}}$$

The PCP discharge to land from wood preserving plants was estimated at less than 1 kkg per year by Versar (1979). The sum of PCP releases from the wood preserving industry as estimated by Versar was 6 kkg per year. This was within an order of magnitude of the 1.6 kkg estimate by JRB.

In addition to plant releases, the PCP released to land as a leachate from utility poles was estimated at 960 kkg per year by Versar (1979), based on an average loss rate of 0.05 lbs of PCP per cubic foot for 42.3×10^6 cubic feet of poles treated in 1974. Table 6.2 shows that $61 \times 10^6 \text{ ft}^3$ of wood were treated in 1975. The average quantity of PCP per cubic foot of wood was derived by JRB as follows:

$$\frac{(\frac{15,000 \text{ kkg}}{60 \times 10^6 \text{ ft}^3})}{(\frac{2200 \text{ lbs}}{\text{kkg}})} = \frac{0.55 \text{ lbs PCP}}{\text{ft}^3 \text{ wood}}$$

The loss ratio was:

$$\frac{(0.05)}{(0.55)} 100 = 9.1 \text{ percent per year}$$

This low ratio indicated that most of the PCP was released to the environment at the end of 12 years or so. JRB feels that it represents a rather high loss rate, but does not have sufficient information for verifying this assertion.

6.4.4.4 Leather Tanning

Versar (1979) estimated that 1 kkg per year was discharged to water, and 3 kkg per year were discharged to publicly-owned treatment works (POTW). The estimate was based on a reported average PCP concentration. However, the number of plants sampled was not reported in the Versar report, and hence no validity could be attributed to that estimate. This release was 8 percent of the JRB estimate of 50 kkg of PCP consumed by the textile industry in the form of sodium salt. In this context, it appeared reasonable.

JRB has assumed that the level of PCP as an impurity in sodium pentachlorophenate was 2 percent. As an upperbound estimate, if half of this PCP salt (25 kkg) was released to land and half to water, the PCP present as an impurity would amount to:

$$\frac{(25.0 \text{ kkg PCP as salt})}{(\text{year})} \times \frac{(0.02 \text{ kkg PCP impurity})}{(\text{kkg PCP as salt})} = \frac{0.50 \text{ kkg PCP impurity to land}}{\text{year}}$$

Similarly, 0.50 kkg was estimated to be released to water. The air release was assumed to be negligible because even if it was assumed to be equal to 0.50 kkg of PCP impurity per year, it is still a small number relative to other sources of PCP air release (e.g., herbicides).

6.4.4.5 Preservation of Adhesive and Textile and Use as a Bactericide

The available literature did not provide adequate information. As an upper bound estimate, half of the PCP salt was assumed to be dispersed to land, and half to water. Then, as in the previous section, 0.50 kkg PCP (as impurity)

was released to land and 0.50 kkg was released to water for each of the three end uses. Those are still small numbers relative to herbicide emissions.

6.4.4.6 Fungicide for Treatment of Sap Stain

The PCP sodium salt was used for this purpose on freshly sawed logs and unseasoned timber, and therefore JRB assumed that the application of the fungicide to the surface area of the wood resulted in near total releases within one year to land and water in equal proportions, or 300 kkg of PCP as the sodium salt to each medium. Since the PCP itself was present as a 2 percent impurity, 6 kkg of PCP as an impurity in the PCP salt was released to land and another 6 kkg was released to water on an annual basis.

6.4.4.7 Fungicide in Cooling Towers

JRB estimated that 5 percent of the sodium pentachlorophenate was released into the air. The quantity of PCP salt released to air was:

$$(700 \text{ kkg}) (0.05) = 35 \text{ kkg PCP salt emitted due to use as a cooling tower fungicide}$$

The quantity of PCP impurity released to air was:

$$(35 \text{ kkg}) (0.02) = 0.70 \text{ kkg PCP impurity emitted due to use as a cooling tower fungicide}$$

Assuming an 80 percent effluent treatment efficiency, the quantity of PCP salt released to water was estimated to be:

$(700 \text{ kkg}) (0.20) = 140 \text{ kkg PCP salt emitted to water due to use as a cooling tower fungicide}$

The PCP impurity is:

$(140 \text{ kkg}) (0.02) = 2.8 \text{ kkg PCP impurity emitted to water due to use as a cooling tower fungicide}$

6.4.4.8 Plywood and Fiberboard Waterproofing

For the waterproofing of plywood and fiberboard, there was no information in the available literature for JRB to estimate releases to the environment. The total amount released should be at the maximum about half of the amount consumed, or less than 600 kkg per year. The estimate was arrived at after considering factors such as leaching from the boards and solid waste disposal in landfills.

6.5 Summary of Pentachlorophenol Materials Balance

The overall summary materials balance is presented in Figure 6.7.

7.0 MAJOR EMISSION LOCATIONS

This chapter will identify geographic sites with a large point source or multiple sources. In order to permit combining data for all chlorophenols into an overall picture, the results are presented in a summary table (Table 7.1).

According to Table 7.1, the most likely point source of multiple chlorophenols was located in Midland, Michigan. Other possible sources of chlorophenol emissions are listed below in decreasing order of possibility.

- Midland, Michigan
- Sauget, Illinois
- Jacksonville, Arkansas; Wichita, Kansas; and Tacoma, Washington
- Portland, Oregon; Niagara Falls, New York; and Verona, Missouri

TABLE 7.1 MAJOR EMISSION LOCATIONS

LOCATION	CHEMICAL COMPOUNDS					
	2-chloro-phenol	4-chloro-phenol	2,4-dichloro-phenol	2,4,5-trichloro-phenol	2,3,4,6-tetra-chlorophenol	Pentachloro-phenol
Midland, MI	X	X	X	X	X	X
Seuget, IL	X	X	X			X(?)
Portland, OR			X			
Jacksonville, AR			X			
Niagara Falls, NY				X		
Wichita, KS				X		
Verona, MO					X	X
Tacoma, WA					X	X

8.0 DATA GAPS

During the preparation of this report, a series of significant data gaps were identified. These are discussed in this chapter and possible methods of obtaining the needed information are suggested.

8.1 IDENTIFICATION OF MAJOR PRODUCERS AND THE ANNUAL PRODUCTION QUANTITIES OF CHLOROPHENOLS

Information on the total production quantities of chlorinated phenols is considered proprietary and is therefore not available. The production quantity is the basis for most of the calculations involved in a materials balance. Without this basis, major assumptions and estimations cannot be verified, and an important uncertainty is introduced into the materials balance study. The most direct way to obtain confidential data on production of chlorophenols would appear to be the TSCA Inventory. This will yield a range of values that would help to confirm estimates made in this report.

8.2 LEVEL OF CHLORINATED PHENOLS CONTAINED IN THE END PRODUCTS AS CONTAMINANTS

No information was available on the amount of a reactant carried over into an end-product. An important example is the possibility of 2,4-DCP contamination in its major end-product, 2,4-D. It is rare for industrial processes to be 100 percent effective in separating products from reactants. If contamination does occur at a considerable level, it could represent a major emission source to the environment.

In order to obtain information on chlorophenol impurities in products, two approaches would need to be used: 1) Information on carry-over of chlorophenols

into non-pesticide products would be sought through communications with producers and consumers, and through a search of the primary analytical chemistry literature (probably via a Chemical Abstracts search). 2) Confidential information on pesticide compositions would be requested from Office of Pesticide Programs through appropriate administrative channels. As described in Section 3.4.4, the procedure would be to obtain the registration numbers of pesticide products derived from chlorophenols, then request confidential information (if available) on chemical analysis of the products. In addition, Dr. Phil Kearney of U. S. D. A. should be located and interviewed. Dr. Kearney was identified by a spokeswoman at Dow Chemical as an authority on impurities in pesticides.

8.3 INFORMATION ON ENVIRONMENTAL EMISSIONS

Little information was available on emission of chlorinated phenols to air, land, and water. Due to the lack of information it was difficult to properly assess emissions of chlorophenols during the various processes. Many best-guess estimates of emissions based on assumptions unverified by data were required in this report. In order to solve this problem, monitoring data on chlorophenol releases to air and water could be obtained and made available. This would not be inordinately difficult because of the small number of plants involved. In fact, it is possible that raw data on emissions at Midland, MI, and Sauget, IL (the two major synthesis sites) already exist but have not been calculated and analyzed. Likely sources for water emissions would be the repositories of NPDES monitoring data in state offices of approved programs or EPA regional offices for non-approved states;

and Effluent Guidelines Division monitoring data on toxic wastes. Since chlorophenols would be expected to be stable in water, samples taken and stored could be re-analyzed. If no monitoring data are presently available, it is recommended that effluent water samples (post-treatment) and downwind air samples be collected at production sites in the order: 1) Midland, MI; 2) Sauget, IL; 3) Jacksonville, AR; 4) Wichita, KS; 5) Tacoma, WA; 6) Portland, OR; 7) Niagra Falls, NY; 8) Verona, MO.

Analytical data on the chlorophenol content of production plant solid wastes would help to test the assumption that land-destined waste from chlorophenol production contains negligible chlorophenols. These analytical data might be obtained from individual plant operators. If not, chemical analysis of sludge samples from each plant would be necessary. Samples should be taken from process solid residues, biological wastewater treatment sludges, and incinerator ash.

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